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WORLD PETROLEUM CONGRESS, London, July 19th to 25th, 1933.

Arrangements are now well in hand for the World Petroleum Congress, which is being organised by the Institution of Petroleum Technologists.

The meetings of the Congress will be held at the Imperial College of Science and Technology, South Kensington, and a Programme giving particulars of the subjects to be discussed has been circulated.

Membership of the Congress is open to all persons interested in the Petroleum Industry, the Membership Fee being 10s.

Apart from the fact that only Members of the Congress will be permitted to attend the meetings and other functions connected with the Congress, they will have the privilege of purchasing preprints of the various papers, and the Report of the Proceedings to be published after the Congress, at a reduced rate.

Full details can be obtained from the Secretary, World Petroleum Congress, Aldine House, Bedford Street, London, W.C. 2.

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Members wishing to indicate their membership of the Institution are reminded that the correct abbreviations as laid down in the By-Laws, Section III., Paragraph 9, are: Hon.M.Inst.P.T. for Honorary Member; M.Inst.P.T. for Member; A.M.Inst.P.T. for Associate Member; Stud.Inst.P.T. for Student; and Assoc.Inst.P.T. for Associate.

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Galley proofs of the paper to be read at a General Meeting are available at the time of the meeting, but members desirous of receiving such galley proofs in advance should apply to the Secretary.

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Medals. The Rodwood Medal is awarded, at the discretion of the Council, as and when desirable, but not more than once each year, to a petroleum technologist of outstanding eminence, irrespective of nationality or membership of the Institution.

A medal and a prize of five guineas is awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented the best paper during the session.

Benevolent Fund. The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

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Prepaid small advertisements, such as situations vacant and wanted, patents for sale and miscellaneous, are accepted at a charge of 1s. per line of seven words (minimum 4s.). Box number 1s. extra. These should be sent to the Associate Editor not later than the 12th of the month in which it is desired they should appear.

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PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. R. Allan has left for Venezuela.

Mr. Kamen Kaye is home from Venezuela.

Mr. F. A. Marr has returned from India.

Mr. G. C. Orr is home from India.

Mr. A. W. H. Phelps has returned from Ceylon.

Mr. J. W. Reid is home from Persia.

Mr. L. S. B. Simeon is returning home from Japan.

The Secretary would be glad to learn of the whereabouts of the following members :—E. E. G. Agius, A. E. C. Corbet, E. J. S. Hewitt and A. MacLean.

LIBRARY.

The following additions have been made to the Library since April 1st, 1933 :—

AMERICAN ACADEMY OF ARTS AND SCIENCES. Vol. 68, No. 1. The Pressure-Volume-Temperature Relations of Fifteen Liquids. P. W. Bridgman.

—— Vol. 68, No. 2. Compressibilities and Pressure Co-efficients of Resistance of Elements, Compounds and Alloys, many of them Anomalous. P. W. Bridgman.

—— Vol. 68, No. 3. The Effect of Pressure on the Electrical Resistance of Single Metal Crystals at Low Temperature. P. W. Bridgman.

—— Vol. 68, No. 4. Radioactivity Measurements. I. The Radium Content of the Keweenawan Basalts and Some Accessory Minerals. II. The Occurrence of Radium, Uranium and Potassium in the Earth. Wm. D. Urry.

BRITISH STANDARDS INSTITUTION. B.S.S. 148–1933. Insulating Oils for Electrical Purposes.

—— B.S.S. 481–1933. Sieves and Screens for Industrial Purposes.

CANADA DEPARTMENT OF MINES. Anhydrite in Canada. Occurrence, Properties and Utilisation. L. H. Cole and R. A. Rogers.

CHEMICAL ENGINEERING AND CHEMICAL CATALOGUE. 9th Edition. 1933.

HEYMAN, LOUIS. The New Aspect of the Oil Problem.

INSTITUTE OF THE MOTOR TRADE. Petroleum and the Modern Motor Car. D. S. Paul.

—— Compression Ignition Engines. C. B. Dicksee.

TULLENERS, A. J. Het Gebruik van Aethyleen en Homologen in de Chemische Techniek.

U.S. BUREAU OF MINES. Tech. Paper, 539. Deviation of Natural Gas from Boyle's Law. T. W. Johnson and W. B. Berwald.

U.S. GEOL. SURV. BULL., 836-D. The Eastern Portion of Mount McKinlay National Park. S. R. Capps.

—— The Kautishna District and Mining Development in the Tatlanika and Totatlanika Basins. F. H. Moffit.

NOMINATIONS FOR MEMBERSHIP OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND FIFTIETH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, London, W.C. 2, on Tuesday, April 11th, 1933, Mr. T. DEWHURST, A.R.C.Sc., F.G.S., President, in the Chair.

The Secretary read the names of candidates nominated for election, and the following list of members elected :—

As Members.—Charles Robert Ghick Beadle, Rolland Beaumont, Edward Boaden, Kenneth Gordon, Walter Ripley Graham, Walter Basil Heaton, Petrus J. Roelfsema, Jocelyn Field Thorpe, Frans Joseph Gustav Vingerhoets.

As Transfer to Member.—John Campbell Wright Robb.

As Associate Members.—Cyril Birkin, Oscar Vincent Soane, Edward Stokoe.

The President said before passing to the main business of the meeting he desired to inform members that good progress continued to be made with the preparations for the World Petroleum Congress. As the members knew, His Majesty's Government had expressed their sympathy with the objects of the Congress, and had intimated their willingness to give a reception to the delegates. Moreover, the Foreign Office was requesting the Governments of foreign oil-producing countries to send delegates to the Congress, and a fair number of satisfactory replies had already been received.

In regard to the most important subject of standardization, the International Standards Association would work in co-operation with the Congress, and would hold a meeting in London during the Congress week. Support would also be forthcoming from Dr. R. P. Anderson, of the American Standards Association, from Dr. L. Ubbelohde, of the International Petroleum Kommission and from the British Standards Institution. The President of the American Petroleum Institute had accepted an invitation to become an honorary member and guest of the Congress, while Dr. Bergius would take the chair at meetings of the Hydrogenation Section.

A very detailed programme of the sessions had been drawn up and would be published very shortly. A Ladies' Committee had recently been formed to arrange for the entertainment of the wives of delegates attending the Congress.

Owing to the great importance of the Congress, there would be no general meeting of the Institution in June of this year. Indeed, Council had decided that the May meeting should be devoted to the Congress, and that the Chairman of the Executive Committee, the Chairmen of the various Sub-Committees, and possibly the Chairmen of sections would explain the position as at the date of the meeting.

The main business of the present meeting was to hear a paper by Messrs. Saal and Verver on "An analytical steam distillation for measuring the volatility range of lubricating oils and other high-boiling petroleum fractions." Mr. Verver had crossed from The Hague with the object of reading the paper, but he had just telephoned to say that he was indisposed and desired the meeting to accept his apologies for his enforced absence. In those circumstances the Institution was very fortunate in that Mr. J. S. Jackson had undertaken to read the paper.

The following paper was then read :—

An Analytical Steam Distillation for Measuring the Volatility Range of Lubricating Oils and Other High-Boiling Petroleum Fractions.

By R. N. J. Saal and C. G. Verver.

Various excellent methods exist for expressing the volatility range of the lower petroleum products (gasolines, kerosines and gas oils), either in the form of well-standardised, empirical distillation tests (such as the A.S.T.M. methods D86–31 and D158–28), or of equilibrium distillation methods. So far, the same cannot be said for the higher-boiling constituents of petroleum (lubricating oils, waxes, etc.). This state of affairs is no doubt largely due to the fact that in the past very little need has been felt for an exact knowledge concerning the volatility of these materials, since they have been mainly sold to viscosity, flash point, colour, melting point and similar properties.

Recently matters have seemed to be changing in this respect. Various investigators have, for instance, very rightly come to regard the volatility range as one of the fundamental properties of a lubricating oil for internal combustion engines. Bahlke, Barnard, Eisinger and FitzSimons[1] have shown that engine carbon formation is largely dependent upon the "high-boiling" constituents of the lubricant employed; they suggest employing the

[1] *S.A.E. Journal*, 1931, **29**, 215-222.

90 per cent. point on a distillation curve (obtained by a method of their design) as an index for the carbonising tendency of the oil.

The volatility of the lubricant may be of importance in all cases in which elevated temperatures prevail. It is, of course, of special interest in the case of steam cylinder oils; it has actually been shown in practice that only those oils which contain a certain proportion of high-molecular constituents are capable of forming an uninterrupted lubricating film in engines employing superheated steam.

Several analytical distillation methods have in the last few years been suggested for expressing the volatility range of lubricating oils in figures, and some of these are actually in use in petroleum laboratories. These tests are almost exclusively vacuum distillations, carried out under various empirical conditions.

After studying the matter carefully, the authors have come to the conclusion that there are several serious objections to an analytical *vacuum* distillation for the purpose in view. These objections are based on the assumption that a good distillation test should be so designed as to avoid decomposition (cracking) of the constituents of the oil as far as possible:—

(1) It will be shown that lubricating oils of various origins commence to show signs of decomposition between 320 and 350° C.; at 375° C. cracking is already very noticeable. In a distillation test the oil should at all events not be heated above 350° C. The heavier lubricating oils will generally contain fractions having molecular weights of 600–700 or higher, and we shall later demonstrate that it requires a diminished pressure of approximately 0·2 mm. Hg to distil over these fractions at 350° C.

Pressures of the above order (and very much lower) are, of course, commonly used in the laboratory, but are not at all suitable for an analytical or standard distillation method. In the first place it is extremely difficult to keep such pressures constant (say, to within 10 per cent.).[2] In the second place, a pressure reading taken *behind* the condensing stage is no reliable measure of the pressure *on the surface of the boiling liquid* if the vacuum employed is at all high. The

[2] This is true in particular for extremely high (cathode) vacua. Although distillation methods employing such pressures, therefore, may be an excellent means of separating an oil into fractions with a minimum amount of decomposition, they are of little value as standard analytical tests. For this purpose they have the further disadvantage that volatilisation is more in the nature of surface evaporation than of ebullition and that the vapour temperatures observed are therefore no reproducible measure of volatility.

pressure under which the liquid is actually distilling may be very considerably greater than that observed, as a result of intermolecular collision and the resistance of incondensible gas in the apparatus. Recent evidence has shown that many of the boiling points under diminished pressure, reported in organic chemical literature, are entirely erroneous on this account.[3]

From the above (and the results to be subsequently described) it will be clear that attempts to distil over an appreciable percentage of a medium or heavy lubricating oil at pressures of the order of 1 mm. or higher (as employed in most of the analytical vacuum distillations actually proposed for lubricating oils) must inevitably lead to very serious decomposition. If—as in the case of one method known to the authors—the distillation is continued to vapour temperatures of 700° F. (371° C.) and over, the determination is more in the nature of a cracking experiment than of a distillation test.

(2) A second objection to the use of vacuum distillation methods for the analysis of heavy petroleum products is the fact that such tests render the use of *direct* heating almost essential, since these methods entail a variable temperature, and it is well known that the temperature control in a vacuum distillation must be flexible. The authors have arrived at the conclusion that *in*direct heating is a condition sine qua non for the purpose in view. The distillation of a heavy oil must necessarily involve temperatures not far removed from the decomposition limit, and experiments will be described to prove that the decomposition caused by local overheating, when employing a direct supply of heat, is far more serious than might be supposed and may lead to completely erroneous results. Cracking has the effect of diminishing the differences which are otherwise found in the volatility curves of oils.

(3) The usual type of vacuum distillation is of necessity a more or less arbitrary test, giving results depending upon the existing degree of dephlegmation; it therefore requires rigid standardisation if reproducible results are to be obtained.

(4) A vacuum distillation involves somewhat complicated apparatus and requires a fair amount of attention and manipulative skill.

[3] See K. Hickman and W. Weyerts, *J.A.C.S.*, 1930, **52**, 4714–4728.

The authors suggest employing a *steam distillation at a constant temperature* for the purpose in view. If the conditions in such a test are so regulated that :—

(*a*) There is substantially complete saturation of the steam with oil vapour;

(*b*) Practically no dephlegmation can occur; and

(*c*) Heating is indirect, by means of a bath of high specific conductivity,

it is obvious that all the objections mentioned above are eliminated. If conditions (*a*) and (*b*) are fulfilled, the test is no longer a purely empirical one and interesting deductions may be made from the readings obtained. If a heating bath is employed, the liquid being distilled may be maintained at a temperature just below the cracking limit without fear of local overheating.

As a measure of volatility in such a constant-temperature steam distillation, the proportion of steam to oil in the distillate may be employed. At any given moment during distillation, *r*, the ratio

$$\frac{\text{volume of oil in the distillate}}{\text{volume of condensed steam in the distillate}}$$

is given by the relationship $r=\frac{p.M}{18d(1-p)}$, where M is the molecular weight of the oil in the distillate, d its density and p the vapour pressure in atmospheres of the oil in the still at the moment in question (the density of water being taken as unity). By determining the proportions, molecular weights and densities of the fractions, therefore, it is possible to determine the course of p if this is desired. Actually, it will usually be of more practical interest to know the range of $\frac{p.M}{d}$, since the volume of a substance evaporating under certain specified conditions will in general be roughly proportional to this relationship. "r" is a good practical measure of $\frac{p.M}{d}$, the factor $(1-p)$ being generally close to unity.

The results obtained from such a constant temperature steam distillation are conveniently expressed graphically by plotting the volumetric percentages of oil in the distillate fractions (i.e. $\frac{r}{r+1}\times 100$) against the volumetric percentage of the original charge which has distilled over to the points where the cuts were made. In this way a stepped line is obtained (see Fig. 1), but by connecting

the mid-points of the fraction percentages (horizontal steps) a good approximation to the true curve is found. An actual example of the calculation will be given later.

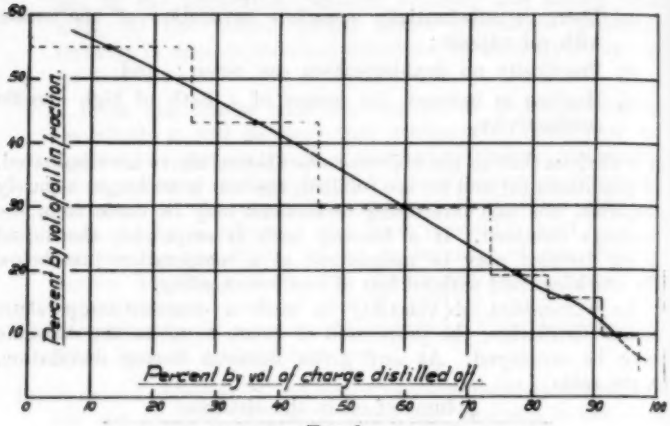

FIG. 1.

GRAPHICAL EXPRESSION OF THE RESULTS OF AN ANALYTICAL STEAM DISTILLATION.

APPARATUS.

Although, as already stated, the results are independent of the conditions under which the test is carried out, as long as conditions (*a*), (*b*) and (*c*), mentioned above, are fulfilled, the apparatus employed by the authors, which is extremely convenient, will be here described. It is illustrated in Fig. 2, whilst the photograph (Fig. 3) shows the more important parts of the equipment.

In Fig. 2, A is an iron still provided with a cover, fitting into it by means of a metal to metal double cone joint, fastened by means of two bolts (inner dimensions of A: abt. 8 cm. diameter and 12 cm. depth). The steam required is raised to slightly above the requisite temperature in superheater C; it is regulated by a needle valve V, and passes through five turns of narrow iron pipe (4 mm. inside diameter) before entering A, where a goose-neck carries it close to the semi-circular bottom of the still. The still, cover and spiral fit snugly into a lagged electric heating jacket B (600 Watts); in the intervening space a low-melting alloy [4] is used for heat transfer. The jacket is provided with a

[4] The so-called Lichtenberg alloy (50 per cent. bismuth, 30 per cent. lead, 20 per cent. tin, m.p. about 92° C.) was used by the authors. Oxidation is not troublesome at 350° C., especially if a little powdered graphite is sprinkled on the surface. 6½ to 7 kgs. of metal are required.

valve for emptying. A small heavy iron pot is a necessary adjunct for drawing off and melting the alloy. A cover, made in two halves, serves to close off the top of the heating jacket. Small projections, visible in the photograph, are welded on to the jacket and still, and are employed, after the fashion of a bayonet point, to prevent the still floating up on the surface of the alloy.

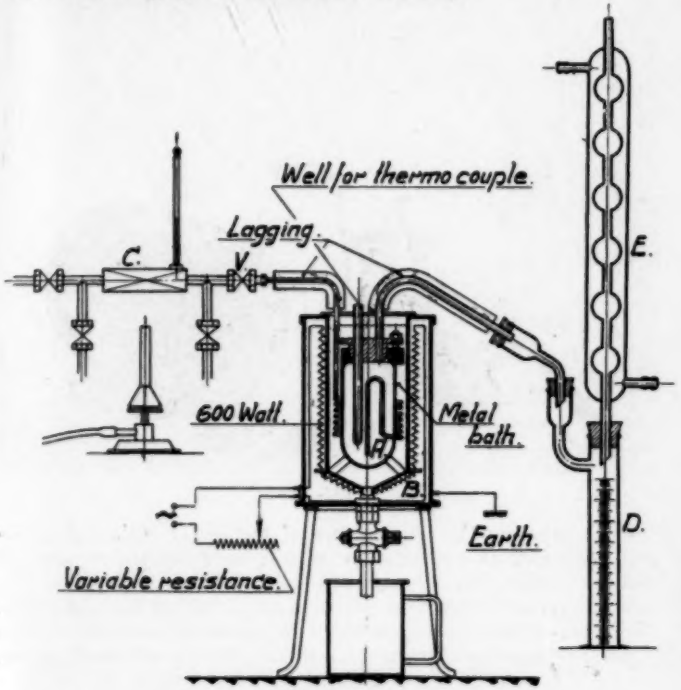

FIG. 2.
APPARATUS FOR ANALYTICAL STEAM DISTILLATION AT A CONSTANT TEMPERATURE.

The cover carries a thermometer well and a vapour tube. The distillate is collected in a graduated cylinder (D), provided with a side tube and condenser (E). This arrangement has the advantage of greatly minimising the formation of resistant emulsions in D, which occur if the condenser is interposed between the still and the receiver.

Theoretically, it would be better if the vapour tube were immersed in the heating bath up to its highest point. A preliminary form

of the apparatus, of a larger size, was actually so constructed, but on a smaller scale this design presented mechanical difficulties. Comparative tests have shown that with proper lagging of the vapour tube practically no condensation occurs.

FIG. 3.

For measuring the temperature of the metal bath and of the still contents, thermo-couples with proper ice-points and an accurate millivoltmeter are strongly recommended, since the distillation ratio is very susceptible to small changes in temperature. The use of ordinary thermometers is only permissible if due attention is paid to corrections for emergent thread, to frequent checking, etc.

PROCEDURE.

The authors employ 320° and 350° C. as standard temperatures for analysing lubricating oils by this method, 300° for distilled and residual paraffin waxes. In the case of lubricating oils, 350° is a convenient temperature for the usual routine purposes, *i.e.*, for the general characterisation of a lubricant or for the estimation of the amount of residual components present. At 350° the distillation of mineral lubricants is approximately 2½ times as rapid as at 320°. As will be shown, however, there is a small but definite amount of decomposition at 350°, and if the fractions are to be submitted to delicate criteria (*e.g.*, to molecular weight

determination, for identification purposes), the distillation should not be carried out at a higher temperature than 320° C. It will be found that very little attention need be given to temperature control, and that the temperature of the metal bath need not depart by more than 1° C. from that of the still.

The authors employ a charge of 100 grams of oil (the sp. gr. of which is determined), and add 75 grams of 4 mm. aluminium Raschig rings to promote good contact. Distillation is carried out at a speed of 20–30 min. for 100 ml. of total distillate. It will be shown that saturation is complete under these conditions down to the last two or three ml. of oil. The fractions may be taken as large or as small as desired, as long as enough points are obtained for constructing the curve. In the case of oils which can be distilled completely, care should be observed to collect the distillate in small fractions towards the end, since complete saturation is no longer obtained when less than about 3 ml. remain in the still. In case the meniscus between the oil and water layer in the measuring cylinder is not quite definite, the cylinders may be placed for a short time in a hot-air oven or boiling-water bath. Large drops of oil which cling persistently to the side of the graduate may be freed by means of a piece of wire, but these drops will seldom be found to affect the result appreciably. A minor error, of little practical importance, is caused by the fact that small quantities of viscous oil are retained in the condenser E. Usually, it will be observed that the total of the oil in the fractions amounts to somewhat more than that of the original charge, owing to traces of retained water. The difference (a few millilitres) may, however, be subtracted from the fraction in their proper proportions without appreciable error.

The following example shows the correction and utilisation of the data obtained from a steam distillation :—

Example of figures obtained in an analytical steam distillation.

Charge : 100 gms. of oil ; sp. gr. 15/4° C. = 0·924 ; vol./15° = 108 ml.

Fraction.	Observed Volumes. Oil in ml.	Water in ml.	Corrected Volumes.* Oil in ml.	Water in ml.	% By vol. of oil in Fraction.	Oil in Fraction with respect to charge % by volume.	"Mid Points" of the Fractions. % by vol.
I. ..	29	22	28	23	55·0	25·9	13·0
II. ..	22	28	21·5	28·5	43·0	19·9	36·0
III. ..	31	70	30	71	29·7	27·8	59·7
IV. ..	10	41	9·5	41·5	18·6	8·8	78·0
V. ..	9	51	9	51	15·0	8·3	86·6
VI. ..	7	68	7	68	9·3	6·5	93·9
VII. ..	(3)	(97)	(3)	(97)	—	2·8	(98·6)
Total	111	—	108	—	—	100·0	—

* "Corrected oil" = $\frac{108}{111}$ × "observed oil," rounded off to 0·5 ml.

Fig. 1 shows the relationship of the values in columns 6 and 8.

Residual oils cannot be totally distilled over at 350° in the manner described. It would appear that at present no available method is capable of doing so without decomposition, since surface distillations at actual pressures of 0·001 mm. Hg. and less still leave an appreciable residuum, although it may admittedly be possible to carry the distillation somewhat further with such extremely low pressures than with a steam distillation at atmospheric pressure. The authors continue the steam distillation until the ratio of oil to water reaches 1 to 99. At this ratio the molecular weight of the distillate will be of the order of 600–650, and hence, by the equation on page 339, the partial pressure of the oil will be approximately 0·00027 atm., or 0·2 mm. Hg.

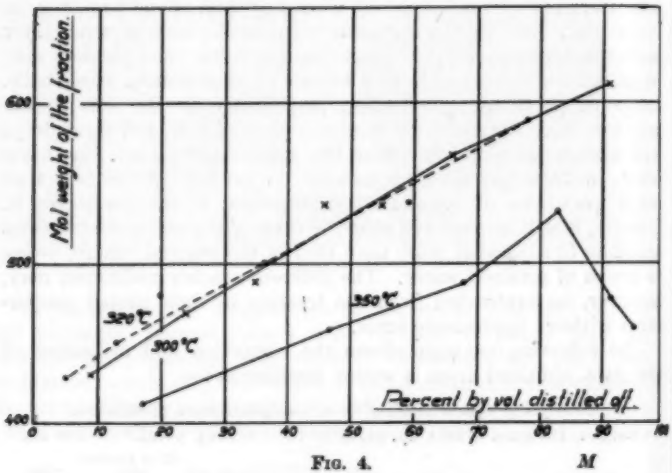

FIG. 4.

RELATION BETWEEN MOLECULAR WEIGHT AND PERCENTAGE DISTILLED OFF OBTAINED IN THE STEAM DISTILLATION OF A VISCOUS VENEZUELAN CONCENTRATE AT VARIOUS TEMPERATURES.

INVESTIGATION OF THE METHOD.

(*a*) *Maximum Permissible Temperature.*—Since it is usually desirable to distil at as high a temperature as possible, the authors, in the first place, set themselves the task of determining the degree of decomposition occurring at various temperatures. This investigation was carried out in two ways:

(1) The molecular weight was taken as a criterium. Oils of relatively narrow boiling range[5] were steam-distilled in the manner described, at 300°, 320° and 350° C., whereupon the molecular weights of the fractions were determined.[6] The following results, which are plotted in Fig. 4, were obtained upon a viscous, concentrated distillate (a cylinder oil for saturated steam) from Venezuelan base material :—

Molecular weights obtained in steam distillations at various temperatures.

Temperature.	Percentages by Vol. distilled off to mid-points of Fractions.	Mol. weight of Fractions.
	5·0 ..	428
	13·2 ..	450
300° C. ..	19·9 ..	480
	36·5 ..	499
	59·5 ..	538
	78·3 ..	589
	9·0 ..	430
	24·1 ..	468
320° C. ..	35·0 ..	488
	45·8 ..	537
	55·3 ..	536
	66·5 ..	568
	91·3 ..	612
	17·3 ..	412
	46·9 ..	459
350° C. ..	68·1 ..	488
	82·8 ..	532
	91·5 ..	478
	95·3 ..	459

Other oils gave very similar results, showing that decomposition is negligible up to 320°, but is noticeable at 350° C.

This, of course, precludes the use of temperatures above 320° in cases where delicate criteria, such as a molecular weight determination, are employed. On the other hand, the drop in molecular weight of the fractions distilled at 350° gives us no information as to the change in the volatility curve produced by the decomposition,

[5] If an oil of wide boiling range is employed, the results are obscured by the alteration in the ratio of the vapour pressures of the components, in the sense of the equation $\frac{d \log.p}{d t} = \frac{Q}{RT2}$, where Q is the molecular heat of vaporisation, R the usual gas constant, T the abs. temp. The lower the temp. the more complete is the separation between a high-boiling and a low-boiling component.

[6] Molecular weights were determined cryoscopically in benzene, observing the precautions mentioned by N. G. Gullick (*J. Inst. Petr. Tech.*, 1931, **17**, 541-571). The values given are those obtained at a depression of approximately 0·3° C., and may be taken as practically identical with those found by exterpolation to infinite dilution.

since it is obvious that a molecule may split up into two portions of very unequal size. The following experiments were carried out to show the effect of distillation at various temperatures on the actual volatility of the oil as determined at 320°.

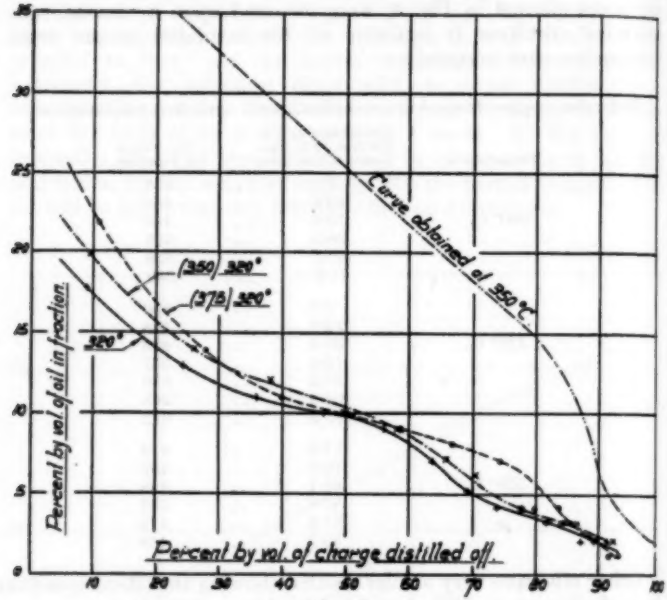

FIG. 5.

VISCOUS VENEZUELAN CONCENTRATE. ANALYTICAL STEAM DISTILLATIONS AT 320° C.

(2) Two oils (the Venezuelan concentrate mentioned above and a turbine oil of Pennsylvanian origin, containing residual components) were steam-distilled at 320°, 350° and 375° C. The fractions obtained at each of the two latter temperatures were then recombined quantitatively (employing pentane, which was later distilled off below 100° C.). The following yields (percentages by weight) were obtained :—

	Venezuelan Concentrate.		Pennsylvanian Turbine Oil.
Distillation at 350°, recombining the fractions	99·7%	..	99·8%
Distillation at 375°, recombining the fractions	98·8%	..	98·9%

The resulting oils were again steam-distilled at 320°, with the following results :—

Analytical Steam Distillation of a Venezuelan concentrate at 320° C. in its original state and after previous distillation at 350° C. and 375° C.

Steam Distillation of original oil at 320° C.				Steam Distillation at 320° C. of oil previously distilled at 350° C.				Steam Distillation at 320° C. of oil previously distilled at 375° C.			
Fraction.	Vol. Oil in Fraction ml. (corrected).	Vol. Water in Fraction ml. (corrected).	"Mid Points" of Fractions (% b. vol.).	Fraction.	Vol. Oil in Fraction ml. (corrected).	Vol. Water in Fraction ml. (corrected).	"Mid Points" of Fractions (% b. vol.).	Fraction.	Vol. Oil in Fraction ml. (corrected).	Vol. Water in Fraction ml. (corrected).	"Mid-Points" of Fractions (% b. vol.).
1	18	82	8·8	1	20	80	9·5	1	22	78	10·5
2	13	87	24·0	2	14	86	25·7	2	14	86	27·2
3	11	89	35·8	3	12	88	38·1	3	11	89	39·5
4	10	90	46·1	4	10	90	48·5	4	10	90	49·5
5	9	91	55·4	5	9	91	57·6	5	9	91	58·6
6	7	93	63·2	6	7	93	65·2	6	8	92	66·7
7	5	95	69·1	7	6	94	71·4	7	7	93	73·8
8	4	96	73·6	8	4	96	76·1	8	4	96	79·1
9	4	96	77·5	9	3	97	79·4	9	4	96	82·9
10	4	96	81·4	10	3	97	82·3	10	3	97	86·2
11	3	97	84·8	11	3	97	85·2	11	2	98	88·7
12	2	98	87·2	12	3	97	88·1	12	2	98	90·5
13	2	98	89·2	13	2	98	90·5	13	1	99	91·9
14	2	98	91·2	14	2	98	92·4	14	1	99	92·8
Residue 8 gms. (8 ml. = 7·8% by vol.).				Residue 7 gms. (7 ml. = 6·7% by vol.).				Residue 7 gms. (7 ml. = 6·7% by vol.).			

Analytical Steam Distillation of a Pennsylvanian Turbine Oil at 320° C. in its original state and after previous distillation at 350° C. and 375° C.

Steam Distillation of original oil at 320° C.				Steam Distillation at 320° C. of oil previously distilled at 350° C.				Steam Distillation at 320° C. of oil previously distilled at 375° C.			
Fraction.	Vol. Oil in Fraction ml. (corrected).	Vol. Water in Fraction ml. (corrected).	"Mid Points" of Fractions (% b. vol.).	Fraction.	Vol. Oil in Fraction ml. (corrected).	Vol. Water in Fraction ml. (corrected).	"Mid Points" of Fractions (% b. vol.).	Fraction.	Vol. Oil in Fraction ml. (corrected).	Vol. Water. in Fraction ml. (corrected).	"Mid Points" of Fractions (% b. vol.).
1	34	16	14·9	1	34	16	14·9	1	36	14	15·7
2	23	27	30·9	2	24	26	40·3	2	25	25	42·5
3	15	35	56·6	3	15	35	67·4	3	14	34	59·6
4	14	86	69·3	4	13	87	69·7	4	13	87	71·5
5	5	95	77·6	5	4	96	77·1	5	4	96	78·9
6	3	97	81·1	6	2	98	79·8	6	2	98	81·6
7	1	99	82·8	7	1	99	81·1	7	1	99	82·9
—	—	—	—	8	1	99	82·5	—	—	—	—

Residue 17 gms. (19 ml. = 16·7% by vol.). Residue 18 gms. (20 ml. = 17·5% by vol.). Residue 18 gms. (20 ml. = 17·5% by vol.)

By plotting the figures, and placing the losses found in the primary distillations before the lightest fractions, three 320° distillation curves were obtained for each oil, *i.e.* :—

A curve on the original oil.
" " oil, previously distilled at 350°.
" " " " " " 375°.

The curves (shown in Figs. 5 and 6) demonstrate that a small but definite amount of cracking occurs at 350°, but that the difference found by predistillation at 375° is much more considerable, the character of the curve for the Venezuelan oil being considerably affected.

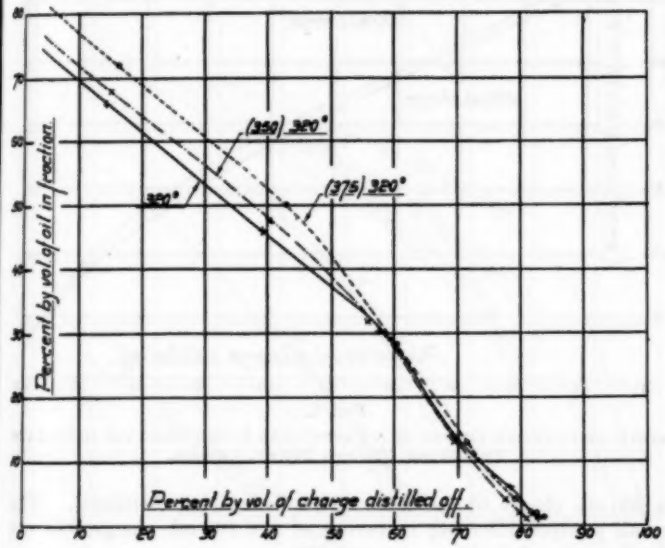

FIG. 6.

PENNSYLVANIAN TURBINE OIL. ANALYTICAL STEAM DISTILLATIONS AT 320° C.

The authors consider that the small amount of decomposition resulting at 350° can be tolerated for ordinary routine work, but that this temperature should be regarded as a maximum. At 350° distillation is, roughly speaking, 2½ times as rapid as at 320°. (See the actual 350-curve for the Venezuelan concentrate, shown as a dotted line in Fig. 5.)

(*b*) *Degree of Saturation.*—Some preliminary experiments had

shown that the shape of the curve obtained is practically independent of the speed at which steam is introduced. This was to be expected, since the degree of saturation will be a function of the time and area of contact between a bubble of steam and the oil, *i.e.*, it will be influenced by the height of the oil in the still. Various experiments with different sizes of charge showed that the results are concordant (*i.e.*, complete saturation is obtained) down to a very small volume (two or three millilitres) of residue in the still. Fig. 7 shows the curves found with a 100 ml. and

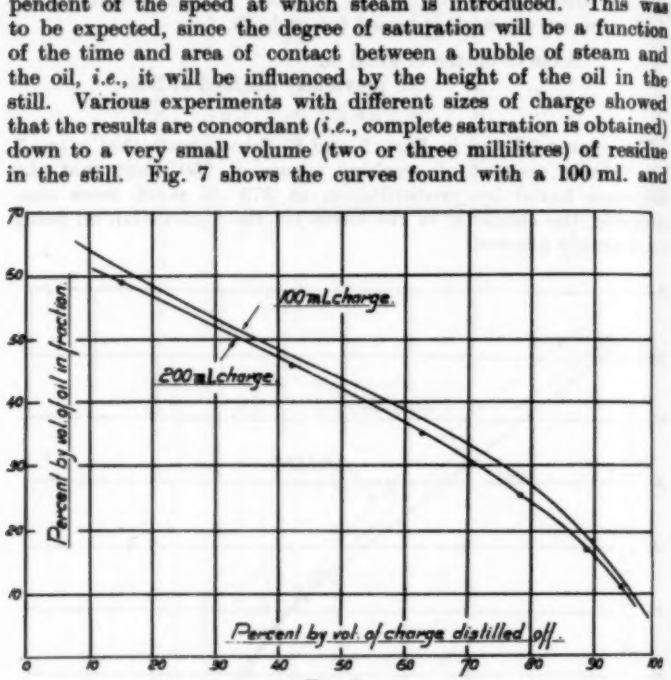

FIG. 7.

STEAM DISTILLATION CURVES OF A VENEZUELAN LUBRICATING OIL DISTILLATE EMPLOYING 100 AND 200 ML. CHARGE.

a 200 ml. charge of the same oil (a Venezuelan distillate). (The small *positive* difference in favour of the 100 ml. charge was not further gone into.)

APPLICATION OF THE DISTILLATION METHOD.

The method has already proved to be of considerable value in all cases where it is desirable to have data on the volatility range of the oil. Some applications which may be mentioned are the following:

(*a*) *Estimation of the Amount of Residual Oil* (*e.g.*, "*Bright Stock*") *Contained in a Lubricating Oil Fraction*.—Since the bright stock and lubricating oil distillates which are currently compounded

to form a commercial oil as a rule have a large overlap in the boiling range, and both components have varying properties, a question as to the relative proportions of these products in an oil is generally unanswerable. It will, however, be possible to proceed by a process of matching, *i.e.*, by comparing the distillation curve of the unknown oil with those of a series of mixtures containing known proportions of a standard distillate and residual oil, and, if necessary, by varying the types of components employed until a satisfactory match is obtained. The unknown oil may then be stated as corresponding in distillation range to a mixture of a per cent. of the distillate oil "A" and $100-a$ per cent. of the residual oil "B."

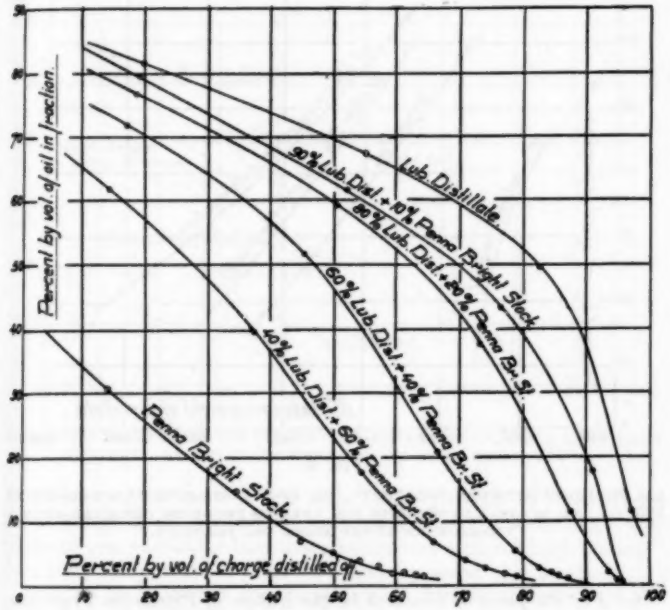
Percent by vol. of oil in fraction
Percent by vol. of charge distilled off
Lub. Distillate
90% Lub. Dist. + 10% Penna Bright Stock
80% Lub. Dist. + 20% Penna Br. St.
60% Lub. Dist. + 40% Penna Br. St.
40% Lub. Dist. + 60% Penna Br. St.
Penna Bright Stock

FIG. 8.

ANALYTICAL STEAM DISTILLATIONS OF MIXTURES OF A VENEZUELAN LUBRICATING OIL DISTILLATE AND A PENNSYLVANIAN BRIGHT STOCK. TEMPERATURE 350° C.

Fig. 8 shows the distillation curves obtained at 350° C. for a Venezuelan distillate (viscosity 60 c.p., or approx. 8·5° Engler at 50° C.), a Pennsylvanian bright stock (209 c.p., or 32° Engler at

50° C.), and 90–10 per cent., 80–20 per cent., 60–40 per cent., 40–60 per cent. mixtures of these components.

(*b*) *As a Check on Fractionating Efficiency.*—Recently considerable attention has been devoted to the sharp fractionation of the higher-boiling petroleum distillates. The steam distillation method may be employed, in the same manner as an A.S.T.M. distillation is used for the lower-boiling fractions, for an empirical comparison of various degrees of fractioning efficiency.

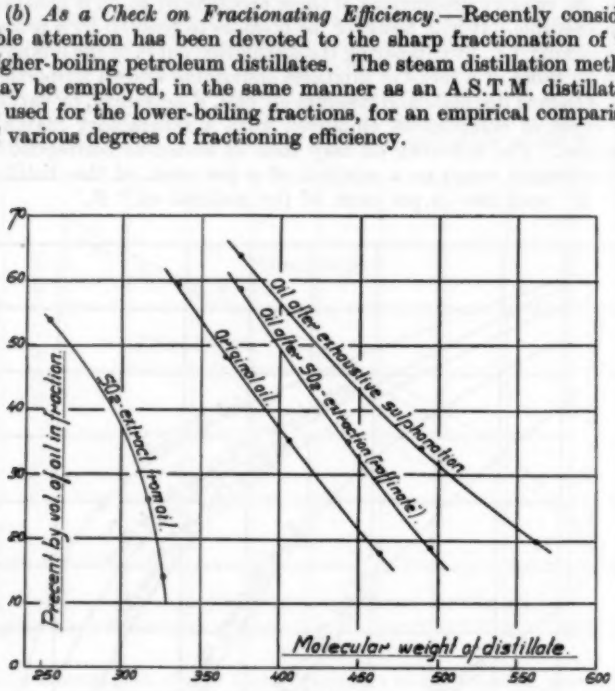

FIG. 9.

RELATIONSHIP BETWEEN VOLATILITY (OIL-UPON-DISTILLATE PERCENTAGES AT 320° C.) AND MOLECULAR WEIGHTS FOR VARIOUS PRODUCTS OBTAINED FROM A VENEZUELAN LUBRICATING OIL FRACTION.

(*c*) *For Purposes of Research on the Nature of Petroleum Fractions.*—The proportion of oil to distillate in a particular fraction, passing over during the steam distillation at a definite temperature, gives a new physical measure, related to the volatility of this fraction. In conjunction with other physical constants, such as specific gravity, molecular weight, refractive index and aniline point, it is found to be useful in the investigation of an oil by enabling these characteristics to be linked up to the volatility range. As an illustration of such a use, Fig. 9 shows the relationship between

the oil-to-distillate percentage at 320° C. and the molecular weight of the fractions for :—

A lubricating oil fraction from Venezuelan base material;
The same oil after extraction with liquid SO_2;
The SO_2 extract of the same oil;
An aromatic-free material obtained by exhaustive sulphonation of the same oil.

The figure clearly shows that a different relationship between volatility to molecular weight exists in each case; the more aromatic the material, the lower its volatility at a particular molecular weight.

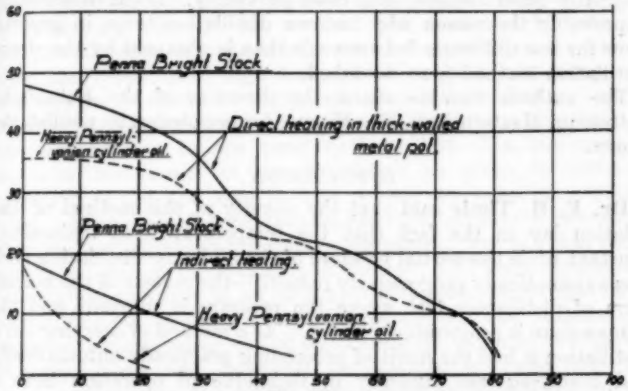

FIG. 10.

STEAM DISTILLATION CURVES OF TWO OILS, EMPLOYING INDIRECT AND DIRECT HEATING. OBSERVED TEMPERATURE IN BOTH CASES, 320° C.

In one or two cases it has been found possible to indentify an oil as being in all probability composed of a "low-boiling" distillate of one particular base material, mixed with a "high-boiling" (residual) component of another origin by using this method.

It is to be expected that considerable benefit will result if the method is coupled with the system of expressing an oil in terms of "the average number of aromatic and naphthenic rings per molecule" (deduced from the specific refraction), as proposed by Waterman and his collaborators.[7]

Finally, it will be of interest to give an example illustrating the absolute necessity of employing indirect heating in a test similar

[7] See a preliminary article by de Vlugter, van Westen and Waterman, *J. Inst. Petr. Techn.*, 1932, 18, 735-750.

to that described above. Fig. 10 shows steam distillation curves obtained at 320° C. for two oils in :—

(*a*) the apparatus described, using the metal bath at a temperature not differing by more than 1° from that in the still;

(*b*) a thick-walled metal pot (wall thickness about 2 cm.), with which it was hoped to avoid the slight objection which might be raised against the use of a molten alloy.

The graph clearly shows that a very considerable amount of decomposition has occurred in case (*b*), in spite of the rapid heat transfer which must have occurred in the walls of the vessel. The decomposition has had the effect of bringing the two curves, originally quite distinct, into close proximity. Local overheating is probably the reason why vacuum distillation tests, in general, show far less difference between oils than is obtained by the steam distillation method here described.

The authors wish to thank the directors of the Bataafsche Petroleum Maatschappij, The Hague, for permission to publish the above.

DISCUSSION.

Dr. F. B. Thole said that the novelty of this method of distillation lay in the fact that the temperature was maintained constant while the partial pressure of the oil in the distillation flask was automatically progressively reduced—the reverse of the normal form of distillation test where the pressure is constant and the temperature is progressively raised. As a method of carrying out a distillation it had the merit of proceeding practically automatically and involving less difficulty in technique of operation than a vacuum fractionation; on the other hand, the resultant curves were on an unfamiliar basis and were not comparable with the usual class of distillation curves.

A more important aspect of the subject, however, lay in the interpretation of the results, for an analysis is not an end but a means to an end—namely, a means of judging either composition or quality in service. The use of this method for judging composition is dealt with in Fig. 8, but the method is only applicable if the distillation curves of the component oils are available. It cannot be used for the more usual problem of investigating the composition of a mixture, the components of which are not known.

It is very doubtful if distillation figures can be used as a means of judging quality in service, for, in spite of the authors' statement that "volatility range is one of the fundamental properties of a lubricating oil for I.C. engines," there is a great volume of experimental evidence in direct opposition to this view. Tests of a number of marketed motor-car oils of good repute, which are

practically indistinguishable as regards excellence of service, have shown them to vary very widely indeed in boiling range. Again, carbon-forming tendencies depend on many of other and more important factors than the 90 per cent. point on a distillation curve.

The speaker was surprised to note the abrupt break in the curve in Fig. 4 at 82 per cent., in view of the fact that the temperature remains unchanged throughout the distillation, and asked if it implied that beyond this point the time of exposure of the remaining 18 per cent. to a mild cracking temperature was for some reason abruptly prolonged. A gradual change of curvature would be expected but a sudden change was curious.

Mr. A. A. Ashworth said the members had been introduced that night to a rather new method of making a steam distillation of lubricating oils, and the method had been put forward for possible adoption as a standard method of distillation in order to show the volatility of high boiling fractions and lubricating oils. He thought it could be recognised that the distillation was an efficient one in that greater percentages of oil were distillable by this method than by the usual methods, but when one came to translate the results of the distillation as given in terms of volatility, it did not seem to convey very much to the ordinary mind. It was said, "Well, that oil had such and such a percentage of water to distillate at a certain temperature," but did that really convey an idea of the volatility of the oil? All were accustomed to recognise volatility as an amount which would be distilled off at certain degrees of pressure and temperature. The authors had indicated roughly some way of calculating the pressure as a partial pressure. They had measured the amount of water and the amount of oil, but the actual partial pressure was based on the assumption that the steam was saturated; and he really failed to see that the authors in their paper had proved that saturation at all. If one looked at the actual circumstances, one had a small still and a very small quantity of oil after one had distilled off 60 or 70 per cent. There were, perhaps, 30 millilitres of oil left in that still. If one looked at the example which was given on page 8, it would be seen that in about half an hour so many millilitres of water as vapour had passed through that oil. The presumption was that the rate of steam passed in was kept fairly constant during the distillation. If that was so, then the velocity of the steam in passing through that small quantity of oil distilled was fairly high. It amounted to 600 cubic centimetres per second. He thought it would be a very bold man, with that 600 cubic centimetres per second passing through 20 or 30 millilitres of oil in the still, who would claim that the steam was saturated with oil vapour. Therefore, when one came to take the measure of water

against the measure of oil as indicating the real partial pressure at which such and such a fraction was distilled, he was afraid one would be widely out of it.

With regard to the special apparatus, he had another little criticism to make—namely, that the apparatus was made for such small quantities that really one would not get fractions large enough to observe other properties than the actual volatility. If the distillation were made with a much larger quantity, one could cut the distillate into fractions and examine the properties of those fractions; but in the present case one was left with a rather peculiar measure of the volatility, and nothing more was obtained from that distillation.

Dr. E. R. Redgrove remarked that most of what he had intended to say about the method itself had already been touched upon by previous speakers. It was a very nice and novel method, and he could quite see that if one had at one's disposal an enormous number of distillation curves of various distillates and residual stocks, one might be able to reproduce a given oil.

Turning to the practical considerations, he said that whilst it was largely true that the amount of carbon that a lubricating oil would form was proportional to the amount of residual stock present, the degree of refinement of all the constituents of the blend was a most important factor. It must be remembered that the distillations described in the paper had been carried out under ideal conditions, where cracking was not allowed to occur, conditions which unfortunately did not prevail in practice, where the oil was all the time being chased up and down the pressure scale, and must suffer an enormous amount of cracking. The curve given in Fig. 9 showing the effect of SO_2 extraction of the oil was most important, and he thought that investigations on those lines might do a lot towards furthering the science of lubrication.

Mr. E. A. Evans remarked that he had been trying to ascertain in his own mind exactly what the objects of the research had been. If it were from the academic point of view, then the method described might be quite useful; but, as Mr. Redgrove had said, if it was going to be used for matching oils, or to try to get some idea of the composition of a blended oil, then he did not think it was a method which was going to be of real help. Certainly one could obtain the results required in an infinitely quicker way. Most people who were associated with the blending of oils had the whole history of the oil when they saw the oil, knew its gravity, its viscosity, perhaps the flash point and the pour test. He respectfully suggested that if these details did not suggest the history, then their experience was somewhat lacking. Therefore, he did not think it was necessary to use this steam distillation

method. In any case, as Mr. Redgrove had already said, one would have to have an infinite number of distillation ranges in order to be able to ascertain what the oil was. After all, in blending oils one was very often largely controlled by the price, and often a quantity of a cheaper oil of the same viscosity was added, and he could not see that was going to be revealed by the author's method.

Mr. Ashworth had criticised—constructively, if he might say so—the mechanism of the process. Personally, he did not think it mattered the least little bit whether the authors were right or wrong; they were offering an analytical method, and the only thing that mattered so far as he could see was whether one could reproduce the results and whether it was going to give one any analytical data to assist in the end. It did seem to him unfortunate that when people had something to say they did not just say it and leave the other parts out.

Dr. Thole had mentioned that the authors were trespassing on very controversial ground when they referred to the high boiling constituents which were liable to increase the carbonisation. Personally, he thought it was a most controversial side, and he did not see how anybody at the present stage could offer any views on it. Then the authors went on to say that it was of special interest in the case of steam cylinder oils. Nicola, the chemist to the Belgian State Railways before the War, had done quite a lot of work on that subject and had designed a cumbersome piece of apparatus, which was expensive and very hard to work. It was based on exactly the same principle but it failed, because fundamentally practically all types of lubrication of steam cylinders were based upon oil being vapourized or atomized with the steam, and not fed in liquid drops direct to the piston. It was almost like upper cylinder lubrication, where one puts a little oil in the petrol hoping that the oil would hit the cylinder wall sometimes, not worrying whether it was the volatile portion or the non-volatile portion which hit the cylinder. Again he thought the authors were trespassing on ground which might just as well have been left out.

Dr. F. H. Garner felt that the arguments in favour of vacuum distillation as an analytical method were much stronger than those mentioned in favour of steam distillation. As had been pointed out by previous speakers, the figures obtained by steam distillation were to a certain extent meaningless owing to the elimination of temperature measurement. The apparatus which was necessary for vacuum distillation at the present time was not in reality much more complicated than that described in the paper. The still itself might indeed be much simpler than that used by the authors, although admittedly the apparatus for maintaining a uniform

vacuum was somewhat complicated. A relatively simple form of apparatus was devised by Dr. Dean and his colleagues at the U.S. Bureau of Mines in a comprehensive survey of the characteristics of United States crude petroleum (Bureau of Mines Bulletin, 207). This apparatus was used by the speaker in a paper read before the Institution in 1921, for the distillation of various lubricating oil fractions from Texas and Pennsylvania crude, including also cylinder stocks. At a pressure of 4 mm. in one cylinder stock 25 per cent. distilled over at 300° C., and 10 per cent. over at 325° C. in the case of another very heavy cylinder stock, and at these temperatures no appreciable amount of cracking occurred.

Another point was that vacuum distillation is used largely in actual practice to-day, and the method of steam distillation outlined in the paper had relatively little value in so far as making available data required in connection with the design of distillation equipment for the production of lubricating oils.

It is well known that steam distillation gives wide cuts as compared with distillation in which the steam is eliminated altogether or kept to an absolute minimum, and it would therefore be of interest if a few more details were available in connection with the statement that the method described in the paper was used as a check on fractionating efficiency.

Mr. E. M. Shipman said he had been very interested in the apparatus described by the authors, and had been wondering whether Mr. Jackson would tell the members of any results which he might have obtained from a similar type of apparatus which he had suggested to him and which he might have tried at his laboratories. He thought possibly, from an observation of it only, that it would give more constant results than the authors' apparatus, in that the hydrocarbon being distilled was contained within its own vapour, and therefore the reflux action was cut out entirely. He had tried himself obtaining boiling points with a similar type of apparatus to the one shown by the authors, excepting that he had used a high-boiling oil in the oil-bath and had lagged the distillation tube as well as he could ; but he had found, even so, that the boiling temperature had not been reproducible accurately on every occasion, and he felt that the apparatus which he had first mentioned might overcome that difficulty.

There was one point with regard to the bath. The authors used a molten metal bath giving a high conductivity, and they employed a vacuum distillation. Now, when the amount of the oil got to a very small quantity, such as the last 10 per cent., the heat was being transferred by that high temperature bath through a fairly high vacuum. Therefore the heat transfer would be

chiefly by radiation rather than by conduction, and he had been wondering if Mr. Jackson could discourse on that point.

A practical point with regard to the cracking of the lubricating oils was the following. The authors showed how lubricating oils were cracked at temperatures of 350°C. Therefore, and referring also to what the last speaker had said, when one had in a compression ignition engine temperatures of 1000°C. and high pressures as well, one had such ideal conditions for cracking lubricating oils that it seemed to him that one wanted the distillation curve of the cracked lubricating oil rather than the steam distillation of it, in order to get the practical results which would show the behaviour of the oil under practical conditions rather than under laboratory conditions. Presumably in an engine, after the lubricating oil had cracked at those high temperatures and pressures in the cylinder, the distillate would dilute the residue of the oil considerably. That was a problem about which internal-combustion engineers were very worried, with regard to the dilution of the lubricating oils by the light fuel oils, and one seemed to be obtaining that condition from the cracking of the lubricating oils themselves.

Mr. J. S. Jackson said it was really rather a privilege and a pleasure to occupy the delightful position of being able to answer without any responsibility.

In reply to Dr. Thole, with reference to the kink in the curve of Fig. 4, he could only suggest that there was possibly a time factor which affected the rate of decomposition.

The question of matching, of course, was an extremely difficult one. If one had to contend with two unknowns, it would obviously be a tedious procedure. No one had, however, explained wherein the vacuum distillation offered any advantage in this respect.

With regard to the importance of volatility, the authors really had not made any very definite statement as to the behaviour of the higher boiling fractions; they had merely drawn attention to the fact that other people had expressed views on the subject, and, in view of this, they had felt that a more convenient method of gaining some information on the question of volatility was obviously required.

In reply to Mr. Ashworth, Mr. Jackson felt that the method was more convenient, but not necessarily more convincing. The new method still had weaknesses, but the authors did claim that as the method was more easily controlled it would probably be more accurate. The paper seemed to him to be a very important contribution towards the solution of a very awkward problem. The last 10 per cent. obviously was not distilled if it was a bright

stock, but, on the other hand, the information obtained from that very fact was the information which was wanted, and it was just as useful by difference as by actual distillation.

He agreed with Mr. Ashworth in his remarks about the interpretation of the results. Obviously one had to think in terms of new facts and regard the matter from a new standpoint; but, after all, that, perhaps, was useful as it encouraged one to look at the problem from another angle.

He could not see Mr. Ashworth's difficulties about the quantities of distillates. It did not seem at all a difficult matter to make that still five times as large if it was found more convenient to do so.

He said that, given fractions which were of reasonable bulk, specific gravity, refractive index, viscosity, etc., could be determined, and possibly the chemical composition of the fractions might give information of importance.

In reply to Dr. Redgrove, the authors certainly did not claim to have solved the problem. The same well-known difficulties still existed. It was merely a more convenient way of going as far as one could go by any other method. In order to get an equally reliable method by means of a vacuum distillation, one would have to work at a pressure of something of the order of 0·1 of a millimetre of mercury, and even in the more modern vacuum methods referred to by Dr. Garner this difficulty had not been overcome. Personally, he felt that this was a very important point since at these low pressures a slight variation in pressure had a very important effect upon the course of the distillation.

In reply to Mr. Evans, he did feel that this distillation method, in common with any similar vacuum distillation, would readily reveal the presence of exceptionally large quantities of cylinder stock. This might be of importance in commercial laboratory work.

With regard to the remark made about the controversial aspect of the paper, he thought the authors would have been quite surprised if they had heard the remarks which had been made on that point. He really thought that they had not intended to bring the controversial side into any prominence.

He agreed with Dr. Garner that the usefulness of these particular data in their present form was rather doubtful in connection with practical development. There was much to be said for the vacuum distillation methods which followed the normal course of temperature rise during the distillation in order to get information which was parallel with practical conditions.

As he had said at the beginning, he was not attempting to answer any of the questions too seriously. He would leave that to the authors, who no doubt would communicate written replies.

The President pointed out that the paper which had been read that night was one of the Congress papers, so that there would be an opportunity for further discussion.

The members were much indebted to the authors for the paper, and also to Mr. J. S. Jackson for the very clear way in which he had presented the subject, and for the able manner in which he had dealt with the discussion.

The meeting then terminated.

Messrs. R. N. J. Saal and C. G. Verver wrote in reply as follows: The authors wish in the first place to confirm Mr. Jackson's statement to the effect that it was not their intention to introduce controversial matter into the paper. The method proposed is merely put forward as a new analytical aid in work on the heavier petroleum fractions. In the central research laboratory of the Royal Dutch Shell Group at Amsterdam it has already proved to be extremely useful and flexible in various branches of investigation, latterly also in fields not dealt with in the paper, such as the carbonising tendency of Diesel fuels, the composition of various types of distilled and residual waxes and the suitability of vapour-phase cracking stock.

The references to the importance of the "volatility range as one of the fundamental properties of a lubricating oil for internal-combustion engines" in the second paragraph unintentionally gave rise to a considerable portion of the discussion, but (together with the remarks referring to steam-cylinder oils in the third paragraph) were only meant to suggest fields in which the method might be of use. It may be pointed out, nevertheless, that considerable interest is being displayed in the "boiling range" of motor oils, principally in America, and the authors consider it obvious that it is worth investigating the volatility of substances employed at temperatures at which they partially or completely evaporate.

In the case of oils for steam-cylinder lubrication, the authors have definite evidence to show that volatility is an extremely important criterion. The case may be cited of two heavy oils possessing the same viscosity at 100° C. (about 5° Engler or 37 centistokes), *viz.*:—

(A) The Venezuelan concentrated distillate referred to in the paper; and

(B) A residual steam-cylinder oil such as one of Mid-Continental or Pennsylvanian origin.

Special practical experiments have shown that oil (B) will give full film lubrication at a temperature of 300–330° C., oil (A) at not more than 220° C.—*i.e.*, that there is a difference of 80–110° in the temperature of the superheated steam for which the oil is suitable.

Naturally it is not intended to imply that volatility is the only or, indeed, the most important factor governing the suitability of a lubricating oil. In the case of a lubricant for water-cooled combustion engines, for instance, it probably plays a relatively minor rôle. Admitting, however, that volatility is a factor worthy of consideration, it must be obvious that gravity, viscosity, etc., do not give the whole history of an oil (as suggested by Mr. Evans) —although they are certainly valuable indices for identification purposes—since these properties may be almost identical for a wide or a narrow cut.

Several criticisms (Dr. Thole, Mr. Ashworth, Dr. Garner) were raised against the unfamiliarity of the system in which volatility is expressed, and the use of constant temperature and variable partial pressure versus constant pressure and variable temperature. The former point is merely a matter of getting accustomed to a different form of curve. With regard to the latter objection, it should be pointed out that a distillation at a pre-determined constant temperature is usually more interesting from a practical point of view than a distillation with a variable temperature. Actually the same applies to the lighter fractions (spirit and kerosine); it was in fact suggested some time ago to carry out constant-temperature (equilibrium) distillations on motor spirits. (See, for instance, James, *J.S.A.E.*, 1926, **18**, 501–507, and the summary given in Engineering Research Bulletin No. 14 of the University of Michigan.) It is only as a result of wide experience that data on dew-point, gas-lock troubles and starting facility can now be deduced from the familiar A.S.T.M. curve in an empirical manner.

Dr. Garner stated that steam distillation gives wide cuts. Actually this is not a specific property of a steam distillation, although this method of distillation admittedly gives wider cuts in a fractionating column than a distillation without steam at atmospheric pressure (owing to the greater dilution of the oil vapours, and the consequent diminution in the scrubbing effect). A steam distillation is in effect identical with a vacuum distillation at the same temperature and at a pressure equal to the partial pressure in the steam distillation. In the present test, all fractionation has been studiously avoided, in order to facilitate calculations and to render the distillation less empirical and more reproducible. The reproducibility is extremely good, if the temperature is kept properly constant. This can seldom be said of a vacuum distillation, as a result of the serious objections which the authors have summed up on pages 338 and 339.

Since the method proposed is intended mainly for research work, and not primarily as a quality measure for lubricating oils, the

deliberate introduction of cracking, as proposed by Mr. Shipman, does not strike the authors as desirable. In any investigation an effort must be made to disentangle the various factors affecting a practical result as far as possible.

For the "matching" of an oil containing residual components it is not necessary to have at one's disposal an enormous number of distillation curves, as suggested by Mr. Redgrove. For a first approximation a set of curves as shown in Fig. 8 of the paper are sufficient, and if divergences are still found, it is a relatively simple matter to choose components (distillate and bright stock) of different volatilities until an accurate match is obtained.

Dr. Thole drew attention to the maximum found in the 350° C. curve in Fig. 4 at approximately 82 per cent. It should be remembered that the rate at which oil passes over decreases as the distillation progresses, so that the opportunity for decomposition increases. The dotted curve in Fig. 5 is the actual distillation curve for the same oil at 350° C., and also shows a somewhat sudden diminution in the speed of distillation between 80 and 90 per cent.

Finally, a few words may be said with regard to the degree of saturation, which was discussed by Mr. Ashworth. It is indeed somewhat surprising that the steam should be saturated with oil vapours down to an oil volume of 3 millilitres in the still. A series of preliminary experiments made by one of us (Dr. Saal) in order to investigate this point, and the results shown on page 350, leave no room for doubt that such is actually the case. It must be repeated that the saturation has little to do with the speed at which steam passes through the oil, but is dependent on the time required for a bubble of steam of a given size to rise through the oil, and hence on the height of the oil column. The first apparatus designed had a capacity of 1 litre, and a very much longer column of oil than that existing in the present apparatus. Nevertheless, the curves obtained have remained identical within the small experimental error of the test. Probably the filling of Raschig rings in the still plays an important part in effecting a good contact between oil and water vapour. As stated in the paper, the authors collect 100 ml. of total distillate in 20–30 minutes. At the lower end of the curve (where the distillate is almost all water) this corresponds to at most 200 c.c. of water vapour per sec. (not 600 c.c , as stated by Mr Ashworth). At a 50 oil-to-distillate ratio this figure is halved.

The authors are very much indebted to Mr. Jackson for the very able manner in which he replied to the questions raised.

A Study of the Refining of a Burmah Crude Oil with special regard to the Colour Reversion Characteristics of the Lubricating Oil Distillates.*

A. R. Bowen, M.Sc., Ph.D., F.I.C. (Member).

The properties of higher boiling distillates concerning their colour and correlation with the refining conditions are subjects on which there is but little information among the many published petroleum researches. Some valuable work on the colour reversion phenomena of certain kerosines has, however, been put forward.

The following account includes the results of a series of experiments on the refining of Indaw crude oil, with special consideration of the colour reversion properties of the lubricating oil distillates. The work was suggested by Messrs. The Indo-Burma Petroleum Company, Limited, to whom, and also to Professor A. W. Nash, the Author wishes to express his gratitude for permission to publish this account.

A consideration of the previous work, although devoted mainly to kerosines, throws much light on the phenomena of colour reversion problems generally. W. J. Wilson[1] has described Burmah crude oils, and makes the following observations: that Burmah petroleum does not readily undergo decomposition by cracking, so that with ordinary care the oil may easily be distilled down to coke, without any appreciable breaking down of the heavier oils to oils of lower boiling-point, or to gas. However, it is found that in the absence of cracking the character of the distillates, particularly of the lubricating oil fractions, may vary considerably, the more complex molecules being apparently liable, under certain conditions, to undergo a rearrangement of their constitution, which renders them less stable chemically under normal conditions of their practical application. It is well known that several crude oils which contain paraffin wax cannot be made to yield the latter in a crystalline form, except under conditions involving cracking, and consequent sacrifice of a part of the paraffin wax and of the lubricating oil, and probably also a lowering of the quality of the latter to some degree. The Burmah oils from the principal fields, however, are stated to yield wax which can be readily filtered from the distillates, partially amorphous wax being obtained only when the distillation of the crude is taken beyond the usual stage. Wilson states, also, that lubricating oils occur usually in somewhat small proportions in Burmah crude oils, and, apart from their relatively high specific gravity, these oils possess no unusual characteristics.

* Paper received February 28th, 1933.

[1] *J. Inst. Petr. Techn.*, 1924, **10**, 227.

J. A. Carpenter[2] has described some interesting observations on the colour reversion of Burmah kerosines. In discussing the unstable compounds in kerosine fractions, this investigator states that untreated kerosine fractions from 180° C. upwards begin to exhibit the phenomenon of fluorescence in increasing degree, together with a tendency to revert in the dark and in bright sunlight to a yellow colour, and in the course of his researches on the colour reversion of kerosine, mainly from Burmah, but also from other sources, a few salient facts were noted as follows. An untreated kerosine will revert in the dark to a deep yellow colour, but the liquid remains clear, while a sufficiently acid-treated or bauxite-filtered kerosine will not revert in the dark. In sunlight, the same kerosines, refined or unrefined, will revert strongly with oxidation, the colour becoming yellow, while later on cloudiness appears, and then deposition of reddish-coloured resinous bodies takes place. In diffused light, kerosines which revert in either the dark or in sunlight do not revert as quickly. A dark-reverted kerosine bleaches in sunlight to a perfectly clear, though possibly tinted, solution, at first with no trace of precipitation, but this proceeds to revert in sunlight sometimes very rapidly. Reversion appears to be to some extent catalysed by the reverted bodies formed. Kerosines from which the aromatics and unsaturateds have been removed by drastic treatment still revert slightly, but very slowly, in bright sunlight in air, but not in atmospheres of carbon dioxide or nitrogen. Sunlight reversion is irreversible. When the final boiling point of a cut is below 185–190° C., no appreciable reversion occurs either in the dark or in sunlight unless the fraction has been intentionally cracked. Above this limit there is a very marked and sudden effect, particularly in sunlight. These observations led Carpenter to the conclusion that dark-reversion is due to condensation or polymerisation of bodies already present in moderately small quantities, and that little or no oxidation is necessary to bring it about. The substances causing this type of reversion can readily be removed. Diffused light is not sufficient to promote oxidation, but it has some tendency to inhibit polymerisation of existing unstable compounds. Sunlight-reversion is a more fundamental change and, though a small amount of reversion is possible in the absence of air, the main action is one of oxidation, followed by condensation and polymerisation; a considerable proportion of the oil is affected. Similar effects were observed with American refined kerosines of the highest grades as well as with those from Asiatic sources. Carpenter throws light on the mechanism of these colour reversions by reference to known chemical reactions of such

[2] *J. Inst. Petr. Techn.*, 1926, **12**, 518.

substances as dianthracene, indene, quinones, fulvenes, and substances exhibiting dynamic isomerism.

It is difficult at the present time to speculate on the chemical structure of the substances causing colour reversion in the lubricating oil fractions as so little is known of the chemical structure of the normal component hydrocarbons in these petroleum distillates. The best known series of hydrocarbons as regards the more complex members is the aromatic series, of which many members have been isolated from coal-tar distillates. There is justification to consider that similar higher aromatic hydrocarbons occur in certain crude oils, or at least in distillates therefrom, as many members of this series have been isolated from lower boiling distillates, for example, from Burmah oil distillates. Many higher aromatic hydrocarbons and their derivatives, including acenaphthylene and fluorenone exhibit colour changes in condensation and polymerisation reactions brought about by such agencies as heat and sunlight.

Olefinic substances are undoubtedly also factors in the polymerisation reactions of these distillates. Such substances as the fulvenes have been mentioned already, and the behaviour of the olefines cyclopentadiene[3] or styrene is also of interest on this subject. Cyclopentadiene is polymerised by heating for 30 minutes at 135° C. At 150° C. its rate of polymerisation is greater than that of isoprene. Dicyclopentadiene (α- or β-) changes into cyclopentadiene at 170–180° C. The effect of heating under pressure is to favour polymerisation rather than depolymerisation, as has been shown also with myrcene. Styrene becomes polymerised to meta-styrene by heating under pressure at 200° C., but is changed back to styrene by distillation.

The mechanism of hydrocarbon polymerisations and depolymerisations is well described by C. D. Hurd.[4] The case of indene is given in some detail and is of interest as an example. The polymerisation of indene by heat takes place more rapidly the higher the temperature, but the molecular magnitude which is ultimately attained appears to be lower the higher the temperature. It is apparent that this polymerisation is essentially a low temperature process and, like most chemical reactions, the reaction is hastened by higher temperatures. The effect of too elevated temperatures, however, induces the reverse reactions of depolymerisation. Thus, cracking sets a limit to the size of a polymeric molecule which can exist at any given temperature. The mechanism for the polymerisation of indene has been suggested

[3] B. T. Brooks, "The Non-Benzenoid Hydrocarbons," 1922, p. 260; C. D. Hurd, "The Pyrolysis of Carbon Compounds," 1929, pp. 738 and 746.
[4] *Loc. cit.*, pp. 740 and 747.

to involve the migration of an ethylenic hydrogen and the retention of one double bond in the polymer. Bis-indene may be distilled in a high vacuum, but at atmospheric pressure, distillation gives indene. These examples show the general behaviour of hydrocarbons with a polymerisation tendency.

Experimental.

A distillation of the topped crude was carried out with a small proportion of steam to give a series of distillates, and later, several repeated distillations were carried out on the topped crude with a large proportion of steam to give a further series of distillates. The volumes of steam used can be gauged by the volumes condensed to water which are recorded with the oil-distillate volumes.

Distillation using Small Proportion of Steam.

Still Charge approx. 2 Gal. of Oil (9100 ml.).

Distillate number.	N.1.	N.2.	N.3.	N.4.	N.5.	N.6.	N.7.
Volume of oil in ml. ..	1195	1965	1535	1315	1175	1020	H.O. & wax.
Volume of water in ml.	305	540	470	640	780	850	—
Highest still temperature	250° C.	300° C.	308° C.	340° C.	370° C.	354° C.	—
Sp. gr. of oil fraction at 15° C.	0·846	0·877	0·898	0·918	0·928	0·918	—

It was apparent that some cracking of the heavier oils had taken place in this distillation by the rise to a maximum and then falling off of the specific gravity of the distillates. In the later distillations, where excess of steam was used, this falling off of the specific gravity was not apparent; the specific gravities of the distillates increased progressively throughout the distillation.

The oil fraction N.5 contained the light lubricating oils and oil N.6 the medium lubricating oils. The oil N.5 was redistilled in steam to give three fractions :—

Distillate number.	N.5.A.	N.5.B.	N.5.C
Volume of oil in ml.	230	230	300
Volume of water in ml.	70	40	70
Highest still temperature	275° C.	302° C.	310° C.
Sp. gr. of oil fraction at 15° C. ..	0·904	0·932	0·940

The two lubricating oil distillates N.6 and N.5.C. were refined with 2½ per cent. of sulphuric acid giving the oils N.6.R. and N.5.C.R. respectively.

Distillation using Excess of Steam.

Still Charge Approximately 2 Gallons.

In this distillation the vapours passed through a column 1 ft. 6 in. in height, packed with Lessing rings. The distillation was carried on until the still temperature reached 270° C., the fractions up to and including the medium lubricating oils being collected. The still-head temperatures recorded were about 60° C. below the still temperatures.

Distillate number.	J.1.	J.2.	J.3.	J.4.	J.5.	J.6.
Volume of oil in ml. . .	1570	1970	1730	1030	1120	790
Volume of water in ml.	2450	370	500	1310	3330	4490
Sp. gr. of oil fraction. .	0·8555 at 12° C.	0·8903 at 13° C.	0·9028 at 13° C.	0·9175 at 11° C.	0·9357 at 11° C.	0·9475 at 12° C.

Four such distillations were carried out, each yielding fractions similar to those above. All the corresponding fractions were mixed. The combined distillate of the J.5 fractions containing the light lubricating oils was indexed J.22, and the combined J.6 fractions containing the medium lubricating oils as J.23. The oil J.22 was further divided into four fractions by distillation at 10·5 mm. pressure, 500 ml. giving 42 ml. of fraction J.24 collected between 95°–175° C., sp. gr. 0·9266 at 16° C.; 195 ml. of fraction J.25 between 175–200° C., sp. gr. 0.9290 at 15° C., viscosity 115 secs. Redwood No. 1 at 70° F.; 124 ml. of fraction J.26 between 200–225° C., sp. gr. 0·9320 at 17° C., and a residue J.27, sp. gr. 0·9413 at 18° C.

Similarly the oil J.23 was divided up by distillation at a pressure of 12·5 mm. into: 65 ml. of fraction J.28 collected between 100–225° C., sp. gr. 0·9430 at 10° C.; 190 ml. of fraction J.29 between 225-240° C., sp. gr. 0·9434 at 12° C.; 170 ml. of fraction J.30 between 240–275° C., sp. gr. 0·9458 at 12° C.; and a residue J.31.

The oil J.29 was treated with 2½ per cent. sulphuric acid and the refined oil designated J.29.R.

Measurement of Colour of Distillates in Estimation of the Degree of Reversion.

It is well known that the eye of the practised oil technologist is one of the best judges of the colour of a distillate in deciding its degree of reversion. However, for recording purposes the measurement of colour is carried out in a tintometer of such types as the Union or Lovibond. The occasional anomalies which are found to exist between the tintometer reading and the visual colour, due possibly to colloidal substances or dichromatism, are capable of making a distillate appear darker to the eye than its tintometer

value indicates. Discrepancies of this kind were only met with in the case of very dark reverted oils, especially with those distillates obtained without the use of steam or vacuum ; the normal coloured oils agreed well visually with Lovibond tintometer readings. With some heavy lubricating oils, a measurement of transmitted light is not sufficient and an estimate of the reflected light (bloom) is necessary. In the examples quoted in this account, it was not found necessary to estimate the bloom of the distillates. All the colours recorded were obtained using a Lovibond tintometer ; the oils, held in $\frac{1}{4}$ or $\frac{1}{12}$ in. cells, using an "artificial daylight" lamp, were matched against the standard colour slides of the yellow (510) and red (200) series. The colour figures in the following account are all expressed with reference to the $\frac{1}{4}$ in. cell.

Standardized Conditions for Colour Reversion.

It was found that a convenient standardized condition for obtaining colour reversion in a distillate was the heating of a small sample for six hours at 210° F. in an open tube immersed well above the oil level in the lead shot of a toluene vapour bath (standard volatility measurement apparatus for transformer and switch oils,[5] Serial Designation T.O. 17). The apparatus was suitably screened from draughts, and care was taken that identical conditions were reproduced in each case.

All such reversion readings were duplicated, and it was found that results were repeatable to a considerable degree of precision.

Characteristics of oils J.22 and J.23.

Oil.	J.22.	J.23.
Sp. gr. at 16° C.	0·930	0·943
Colour unrefined in $\frac{1}{4}$ in. cell (Lovibond) ..	Yellow 7 Red 0·5	Yellow 24 Red 2·0

Both oils were clear and bright, J.22 being very light-coloured and J.23 of good colour for an unrefined distillate. Both distillates retained their good colour on standing for several weeks.

Colour reversion figures on oils derived from (1) *Distillation with small amount of steam—N Series, and* (2) *Distillation with excess of steam—J Series.*

Oil.	Colour. Yellow.	Red.
Oil N.6.R., *i.e.*, N.6 fraction refined with 2$\frac{1}{2}$ per cent. acid ..	15·0	0·9
Oil N.6.R. reverted after 6 hours at 210° F.	51·2	2·8
Oil N.5.C.R., *i.e.*, N.5.C. fraction refined with 2$\frac{1}{2}$ per cent. acid	4·0	0·4
Oil N.5.C.R. reverted after 6 hours at 210° F.	10·0	1·1
Oil J.22.R., *i.e.*, Oil J.22 refined with 2$\frac{1}{2}$ per cent. acid ..	1·0	0·0
Oil J.22.R. after reversion (6 hours at 210° F.)	1·0	0·0
Oil J.23.R., *i.e.*, Oil J.23 refined with 2$\frac{1}{2}$ per cent. acid ..	5.0	0·2
Oil J.23.R. after reversion (6 hours at 210° F.)	5·0	0·2
Oil J.29.R., *i.e.*, Oil J.29 refined with 2$\frac{1}{2}$ per cent. acid ..	2·0	0·2
Oil J.29.R. after reversion (6 hours at 210° F.)	3·0	0·2

[5] *Inst. Petr. Techn.*, "Standard Methods of Testing Petroleum and Its Products," 1929, 2nd edit.

The two oils, J.22 and J.23, were each refined with 2½ per cent. sulphuric acid, the refined oils being designated J.22.R. and J. 23.R. respectively.

The greatest colour reversion is thus shown by the refined distillates from the original distillation where little steam was employed, while all oils derived from the lubricating oil distillates, from the original distillation where the steam/oil ratio used was about 3 : 1, showed little if any colour reversion under the standardized conditions.

Comparative reversion figures on three commercial refined oils of similar viscosity.

Oil.	Colour. Yellow.	Red.
Light lubricating oil	8·0	0·5
Ditto reverted after 6 hours at 210° F.	11·2	0·7
(1) Spindle oil (American), sp. gr. 0·890 at 15° C.	4·0	0·2
Ditto reverted after 6 hours at 210° F.	8·0	0·5
(2) Spindle oil (American), sp. gr. 0·895 at 15° C.	4·0	0·5
Ditto reverted after 6 hours at 210° F.	9·0	1·1

The Possible Inhibition of Reactions that Cause Colour Reversion.

The type of colour reversion taking place under the standardized reversion conditions described in this paper was of the dark-reversion type—*i.e.*, due to polymerisation or condensation reactions. This was shown by reverting distillates in air and in atmospheres of nitrogen when similar colour readings were observed. During this colour reversion a change in specific gravity took place—*e.g.*, the oil N.6.R. increased in specific gravity (at 17·5° C.) on being heated for 6 hours at 210° F. from 0·9108 to 0·9219. The action was tried of a number of substances on the colour reversion of distillates, especially those of the latter showing marked reversion of colour. Among these substances tested were aniline, o-cresol, oxalic acid and alcohol, but no appreciable change in the degree of colour reversion was noted. The sunlight or oxidation type of reversion would undoubtedly be more affected by catalysts and inhibitors than the dark-reversion type. As regards oxidation reactions generally, lead tetraethyl,[6] certain aromatic amino, phenolic, and nitro bodies,[7] including resorcinol and

[6] H. L. Callendar, R. O. King and E. W. J. Mardles, E.P. 295,230; *cf. Rev. Petr.*, Nov. 10th, 1928, p. 1581; S. Hatta, *J.S.C.I.*, Japan, 1925, **28**, 1346.

[7] R. T. Haslam and P. K. Frolich, *Ind. Eng. Chem.*, 1927, **19**, 292; G. Egloff, W. F. Faragher and J. C. Morrell, U.O.P. Booklet No. 79; G. Egloff, J. C. Morrell, C. D. Lowry and C. G. Dryer, *Ind. Eng. Chem.*, 1932, **24**, 1375; W. H. Thomas, *J. Inst. Petr. Techn.*, 1932, **18**, 350; W. H. Hoffert and G. Claxton, *J.S.C.I.*, 1933, **52**, 25T.

hydroquinone,[9] are examples of substances that have inhibitory action in various oxidation processes, but there is little evidence that such substances would be of value in inhibiting the polymerisation and condensation reactions occurring during the dark-reversion of oils. However, hydroquinone has been suggested as a stabiliser to prevent the polymerisation of styrene during distillation at atmospheric pressure.[9]

At ordinary temperatures it appears that many polymerisation reactions are favoured. In discussing this point, P. Sabatier[10] states that depolymerisations are far more rare than polymerisations, since the polymers usually correspond to a much more stable molecular state. Inhibition of such polymerisation or condensation reactions is a subject on which there are very scanty facts. E. K. Rideal and H. S. Taylor[11] classify inhibited reactions into (*a*) reactions inhibited by reduction of the concentration of a positive catalyst; (*b*) reactions inhibited by reduction of the concentration of a reacting constituent; and (*c*) reactions inhibited by diminution of a chain of reactions in which activating energy is produced. Far more is known about catalysts for polymerisation, and included among these are such substances as sulphuric acid, zinc chloride, boron trifluoride, anhydrous aluminium chloride and metallic sodium[12] or potassium, all of which have been studied with regard to petroleum and its products. It was concluded that the search for possible inhibitors to prevent the dark-type reversion of oils presented a problem worthy of future investigation.

The Action of Ultra-Violet Light on Reverted Distillates.

A characteristic of some dark-reversions is the fact that sunlight or ultra-violet light has an initial bleaching and depolymerising action. This is well shown by the action of ultra-violet light on a sample of reverted oil N.6.R. in a quartz flask exposed to the air.

	Colour. Yellow.	Red.
Original oil N.6.R.	15·0	0·9
Oil N.6.R. reverted after 6 hours at 210° F.	51·2	2·8
Reverted oil N.6.R. exposed to U.V.L. for 1 hour	32·0	2·0
Reverted oil N.6.R. exposed to U.V.L. for 2 hours	32·0	1·8
Reverted oil N.6.R. exposed to U.V.L. for 6 hours	40·0	2·5

[9] B. T. Brooks, *Ind. Eng. Chem.*, 1924, **16**, 185.

[9] C. D. Hurd, *loc. cit.*, p. 739.

[10] P. Sabatier and E. E. Reid, "Catalysis in Organic Chemistry," 1923, paragraph 234.

[11] E. K. Rideal and H. S. Taylor, "Catalysis in Theory and Practice," 1926, p. 144; *cf.* The Chain Reaction Theory of Negative Catalysis. H. L. J. Bäckström, *J.A.C.S.*, 1927, **49**, 1460; *Meddel fran K. Vet.-Akad:s Nobelinstitut*, Bd. 6, N:o 15, N:o 16.

[12] U.S.P. 1,865,235; *cf.* J. B. Conant and A. H. Blatt, *J.A.C.S.*, 1927, **50**, 542 and 551.

The prolonged action of ultra-violet light was to revert the oil again in colour by, presumably, oxidation processes.

Solvent Extraction of Lubricating Oils and Colour Reversion Properties of the Hydrogen-rich and Hydrogen-poor Fractions.

Liquid sulphur dioxide, saturated solutions of sulphur dioxide in acetone and many organic solvents can be used to divide an oil into hydrogen-rich and hydrogen-poor fractions.[13]

Sulphur Dioxide Extraction of Oil N.5.C.R.

This oil was washed with liquid sulphur dioxide and a 16 per cent. extract separated. All traces of the solvent were removed from the extract and washed oil, and the latter were submitted to the standard reversion conditions. The sulphur dioxide extract, designated oil N.5.C.R. 2, was a viscous oil of sp. gr. just over 1, and of empirical formula C_nH_{2n-16}. (The oil J.29.R. had an empirical formula of C_nH_{2n-8}) :—

	Colour. Yellow.	Red.
Original oil N.5.C.R.	4·0	0·4
Ditto reverted after 6 hours at 210° F.	10·0	1·1
Sulphur dioxide washed oil (N.5.C.R.1)	4·0	0·5
Ditto reverted after 6 hours at 210° F.	6·0	0·9
Sulphur dioxide extract oil (N.5.C.R.2)	14·0	1·4
Ditto reverted after 6 hours at 210° F.	22·5	2·4

The extraction of other oils with sulphur dioxide and sulphur dioxide/acetone mixtures gave similar results indicating that the substances largely responsible for the colour reversion of distillates can be concentrated in the hydrogen-poor, high specific gravity, extract.

Possible Origin of a Part of the Colour Reverting Bodies in the Distillates. Significance of the Asphalt and Resin Content of the Crude Oil.

The topped crude under examination contained only a very small amount of asphalt, but contained also a small amount of resinous substances that can be removed by treatment of the oil with a refining earth. A sample of the topped crude was given a 25 per cent. treatment with "Corona S." refining earth for 20 min. at 60° F., and on filtration gave the "earth-treated" crude oil. The resinous material retained by the refining earth was extracted with chloroform, freed from the solvent, and added to another sample of the topped crude oil, giving the "resin-enriched" crude oil.

[13] W. J. Wilson and B. C. Allibone, *J. Inst. Petr. Techn.*, 1925, **11**, 177.

The two oils were submitted to a distillation to 300° C., at atmospheric pressure followed by a distillation at a pressure of 7·5 mm. to 320° C., the vacuum distillates being used for the following tests :—

Oil J. 13 was the vacuum distillate from the " earth-treated " oil, and oil J. 16 the vacuum distillate from the " resin-enriched " oil.

The two oils J. 13 and J. 16 were submitted to colour reversion tests.

Oil.	Colour. Yellow.	Red.
Oil J.13, original colour	8·0	0·5
Oil J.13 reverted after 6 hours at 210° F.	10·0	0·7
Oil J.16, original colour	20·0	1·6
Oil J.16 reverted after 6 hours at 210° F.	30·0	2·0

The resin-enriched oil thus gave distillates of decidedly inferior colour to the earth-treated crude oil, and the experiment indicates that badly reverting distillates could be formed by the heating of the heavier ends of the crude oil to about 320° C.

Distillation Conditions and the Effect on the Colour Stability of the Distillates.

A comparative series of vacuum distillations was carried out on an untreated spindle oil fraction which had been originally obtained from a distillation where little steam had been used and which was comparable with oil N. 5. The distillations were carried out at a pressure of 6–7 mm. of mercury, under as far as possible identical practical conditions; the middle cut representing approximately 50 per cent. of the still charge was collected in each case.

The copper still was charged with 200 ml. of oil, and in the first experiment was directly gas fired. The pressure was maintained about 6 mm., and the middle distillate (100 ml.) collected between the temperatures of 165–225° C. This distillate was indexed C. 2.

In the second experiment the still was heated by means of an oil-bath and under similar conditions as before the distillate C. 8 was collected. By reference to the colour reversion figures given below it will be seen that the use of direct heating of the still was sufficient to cause the formation of some colour reverting substances. Further similar vacuum distillations were carried out, but in these cases with certain additions to the still charge. In one case, 1 per cent. of solid caustic soda was added to the still (2 gms. per 200 ml. oil), the distillate being indexed C. 6, and in the last two cases, additions of refining earth (Corona S. bleaching earth) were

made in approximate proportions of 4 and 20 per cent. respectively (*i.e.*, 8 and 40 gms. per 200 ml. oil), and the distillates obtained as before were indexed C. 10 and C. 14 respectively.

The colour reversions of the unrefined distillates are tabulated below :—

Still charge.	Index No. of distillate.	Colour of distillate.		Colour of distillate reverted after 6 hrs. at 210° F.	
		Yellow.	Red.	Yellow.	Red.
200 ml. oil (still gas fired) ..	C.2	20·0	1·6	51·0	4·4
200 ml. oil (still oil-bath heated)	C.8	15·0	1·1	40·0	3·6
200 ml. oil+4·3 per cent. earth (still oil-bath heated)	C.10	15·0	0·45	31·0	2·0
200 ml. oil+21·4 per cent. earth (still oil-bath heated)	C.14	2·5	0·0	10·0	1·0
200 ml. oil+1·1 per cent. caustic soda (still oil-bath heated) ..	C.6	8·0	0·2	10·0	0·6

It is thus apparent that more stable oils as regards colour reversion are obtained from a badly reverting oil by vacuum distillation in the presence of either 1 per cent. of caustic soda or 20 per cent. of refining earth, without the necessity for acid treatment or further refining.

Vapour-Phase Soda Refining of Lubricating Oil.

There are certain disadvantages in the use of soda in a still even if applied suspended in the vapour at the top of the still, the residual oil or coke is liable to contamination. Accordingly stills were designed with side arms or tubes fixed between the still and condenser which may be heated if necessary to prevent condensation. In these tubes the caustic soda was placed preferably on a carrier such as pumice to ensure the maximum surface presented to the vapours.[14] Laboratory scale stills were designed utilising

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[14] Brit. Provisional Pat. No. 36435, Nov. 28th, 1929.

[15] Tintometers and Colorimeters: Lovibond, E.P. 263,924; 277,166; various, E.P. 324,351; 324,495; 299,194. Apparatus and Method for the Determination of the Colour of Mineral Oils, and the Estimation of the Quantitative Relation in Oil Mixtures, S. Szalai, *Petr. Zeit*, 1930, **26**, Motorenbetrieb (7–9).

[16] Photolysis of Mineral Oils, E. Vellinger and P. Marchand, *Ann. des Comb. Liq.*, 1930, **5**, 977.

[17] Spectro-photometer Determination of the Changes that Accompany Deterioration of Mineral Oils, E. Vellinger, *Ann. des Comb. Liq.*, 1931, **6**, 225.

[18] Examination of Asphalt and Tar with the Quartz Analysis Lamp, F. Macht, *Erdöl u. Teer*, 1931, **7**, 225.

[19] A Method of Colour Determination in Mineral Oil Refineries, H. Magnus, *Petr. Zeit.*, 1929, **25**, 984.

[20] Fluorescence in Mineral Oils, J. Tausz and C. Rabl., *Erdöl u. Teer*, 1931, **7**, 106 and 384; *cf.* K. Trautzl, *ibid.*, 193.

[21] Measurement of Bloom of Lubricating Oils, L. M. Henderson and H. C. Cowles, *Ind. Eng. Chem.*, 1927, **19**, 74.

[22] Imparting a Green Fluorescence to Oils: U.S.P.'s 1,708,563; 1,708,592 1,708,602; 1,839,012; 1,842,856; 1,868,473; 1,869,608.

this principle, and comparatively stable distillates as regards colour reversion were obtained.

Summary.

The experimental work indicates that Indaw topped crude oil when distilled with excess of steam, yields lubricating oils of considerable stability as regards colour even in the unrefined state, indicating that vacuum distillation is desirable in producing lubricating oils from this crude.

If, however, the distillation is carried out with only small proportions of steam, distillates are obtained that exhibit colour reversion tendencies, the dark-reversion type being investigated in this work.

In the presence of highly actinic light such as ultra-violet light, a dark-reverted oil is bleached to some extent, but after prolonged exposure to this influence the sunlight-type of reversion takes place.

Inhibitors appear to be of greater potential value in oxidation types of reversion than in polymerisation or condensation types.

Extraction with certain solvents concentrates the major portion of the colour-reverting bodies of a lubricating oil distillate in the hydrogen-poor extract.

The asphaltic and resinous constituents of the crude oil, on being heated to certain temperatures, contribute to the content of colour-reverting substances in a distillate, but the over-heating of a distillate can generate colour-reverting substances also.

The presence of small quantities of solid caustic soda or somewhat larger quantities of a suitable refining earth in the still gives greater colour stability to the distillates. Such agents could be applied satisfactorily to the distillate when the latter is in the vapour-phase.

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The Simplest and Most Accurate Viscometer, and other Instruments with Suspended Level.*

By Professor Dr. L. Ubbelohde (Hon. Member).

Symbols Used.

b = width of layer of liquid (in an open channel).
C_1 = see page 388.
d = depth of layer of liquid (in an open channel).
g = acceleration of gravity.
h = height of liquid column (difference in level, pressure head).
h_1 = loss of head in open channel (see page 385).
k = calibration constant (factor which when multiplied by t gives ν in centistokes).
l = length of the capillary.
l_1 = length of a liquid layer with free surface (in an open channel).
$p = h \rho g$ = loss of pressure.
r = radius.
r_a = radius in a special case (see page 385).
t = time in seconds.
V = volume flowing past a section of the tube.
V_1 = volume flowing past a section of a channel.
α = surface tension or interfacial tension constant.
β = see page 386.
γ = specific gravity.
η = dynamic viscosity in the c g s system = $(l^{-1}\ m\ t^{-1})$.
$\nu = \frac{\eta}{\rho}$ = kinematic viscosity = $(l^2\ t^{-1})$
$\rho = \frac{\gamma}{g}$ = density = $(m\ l^{-3})$.
P = poise = $(l^{-1}\ m\ t^{-1})$, the unit of η.
$cP = \text{centipoise} = \frac{P}{100}$
St = stoke = $(l^2\ t^{-1})$, the unit of ν.
$cSt = \text{centistoke} = \frac{St}{100}$

Introduction.

However completely the viscosity of liquids has been treated since the time of Newton, from the mathematical and the physical viewpoints in the regimes of quiet so-called laminar flow, and also in the turbulent regime, just so incomplete to-day are the instruments used to measure viscosity. Thus, the many values of viscosity in the literature contain errors of larger or smaller size which, unfortunately, cannot now be corrected. For a long time the condition has been especially bad in technical analysis; here it has been considered satisfactory to use instruments and units

* International Petroleum Kommission Publication No. 18,810, dated February 11th, 1933. Translated from the German by Winslow H. Herschel, U.S. Bureau of Standards.

of measurement which were not known to be incorrect, to say nothing of knowing the necessary corrections to apply.

It has been possible for years, by formulas[1] and tables,[2] to convert the conventional values obtained by these instruments into absolute units, so that the instruments are satisfactory for simple mineral oil analysis, but the errors of measurement are often too great with the conventional instruments even to prepare viscosity–temperature curves.[3] It is true there are for such purposes capillary viscometers which give more accurate results, but either they are too costly or the more convenient forms are too inaccurate.

Thus, in spite of much discussion extending over many years in all countries, concerning the selection and standardization of viscometers, no general satisfactory solution could be arrived at; a compromise always had to be made between the two requirements of accuracy and simplicity because no one instrument satisfied both.

Now viscosity, as a constant of the material, is not only of importance in technical analysis, but both it and the phenomena at the boundary surfaces should also be taken into consideration to a much greater extent than previously in pure scientific work; they both have the closest relation to that complex of questions whose ultimate goal is a still unformulated kinetic theory of liquids. Accuracy of measurement is a fundamental requirement for this purpose; but here again the simple instrument is lacking.

In a critical evaluation of many viscometers, which run into the hundreds, the rotation, oscillating and falling ball methods were considered too inaccurate; but also in the case of the remaining capillary viscometers, it was soon recognised that their possibilities of improvement had already been exhausted or had been carried too far, so that it did not appear advisable to introduce further variations.

A phenomenon not previously noted, the suspended liquid surface, was developed into a new physical aid, the "suspended level," which may be used to increase to an extraordinary degree the accuracy of measurements on liquids. It led not only to an entirely new type of viscometer, which is simple and also unsurpassed in accuracy, and to an apparatus to measure capillary

[1] Ubbelohde, "Einige Neuerungen am Englerschen Viskosimeter und Tabellen für das Viskosimeter," *Chem Ztg.*, 1907, **38**; also, "Zur Theorie der Reibung geschmierter Maschinenteile," *Petr. Z.*, 1912, **7**, 773, 882, 938; 1913, **8**, 965. Compare also Mitteilungen der Internationalen Petroleum Kommission, No. 18,627, *Petr. Z.*, 1932, **28** (17), 1.

[2] Ubbelohde, "Tabellen zum Englerschen Viskosimeter," 4th edit. in preparation.

[3] Compare Walther, "Ueber die Auswertung von Viskositätsangaben," *Erdöl u. Teer*, 1931, **7**, 382; also Maschinenbau, 1931, **10**, 670; and "Internationale Tabellen für Viskosimeter" by Ubbelohde, see note 48.

rise, but also to measurements of the dynamic surface tension and to other problems of flowing films which are of great significance in colloid chemistry and biology, and in the study of bearing friction.

I. Available Relative Viscometers.

Summary.—This section contains a review of the principles of capillary measurements and of the method of using relative viscometers, and shows the natural limits of accuracy of these instruments, due to uncertainty in the adjustment of the lower level.

(*a*) *Fundamental Principles.*—For our purpose only capillary viscometers need to be considered, as the rotation, oscillating and falling ball instruments are less exact. For a capillary viscometer the formula of Poiseuille is valid—

$$\eta = \frac{t \pi p r^4}{8 l V} \quad \ldots\ldots (1)$$

Here η is the dynamic viscosity,[4] t is the time of discharge, p the pressure, r the radius of the capillary, l its length, and V the volume of flow. The pressure, p, in most instruments in use, is due to hydrostatic head, the liquid under test flowing from an upper to a lower level; we therefore replace p by $g \rho h$ (g=acceleration of gravity, ρ=density, h=difference in level), and also replace η by $\nu \rho$ (ν=kinematic viscosity), and then we have the formula for kinematic viscosity—

$$\nu = \frac{t \pi g h r^4}{8 l V} \quad \ldots\ldots (2)$$

This formula is valid only as long as the kinetic energy is negligible; otherwise an additional term, the Hagenbach correction,[5] must be added, and it then becomes—

$$\nu = \frac{t \pi g h r^4}{8 l V} - \frac{m V}{8 \pi l t} \quad \ldots\ldots (2A)$$

We shall need only formula (2) for the present. All other values than ν and t in it are instrumental constants for one and the same instrument, so long as it operates under the hydrostatic head of the liquid, so that—

$$\nu = t k \quad \ldots\ldots (3)$$

[4] The dynamic viscosity η is the force which a surface of 1 cm.^{2} exerts on a parallel plate at a distance of 1 cm. moving with a velocity of 1 cm. per second. When the force is one dyne, the unit viscosity is called a poise (P), the hundredth of a poise being one centipoise (cP). Water at a temperature of 20·2° C. has 1 cP, rape seed oil at 20° C. about 1 P. The kinematic viscosity ν is the quotient $\frac{\eta}{\rho}$, both values taken for the same temperature. The unit of kinematic viscosity is called a Stoke (St), a hundredth of it, a centistoke (cSt). It is named according to the proposal of M. Jakob, *Zeit. f. techn. Physik*, 1928, **9**, 21.

[5] See note 28.

If the calibration constant,[6] k, is not to be calculated from the dimensions of the viscometer but from the time of flow of a liquid of known viscosity, then the viscometer can be made relatively simple. It is customary to call such an instrument a "relative viscometer," and to use equation (3) in calculations. In what follows we shall see what errors are thus introduced.

(*b*) *Pipette Instruments.*—The so-called pipette instruments are among the oldest viscometers, all of which have a bulb and a

FIG. 1.
PIPETTE VISCOMETER.

capillary from which the liquid flows directly into the air (Fig. 1). The pipette is filled, the liquid to be tested is allowed to flow out under its own head, and the time t is determined in which the meniscus falls from mark m_1 to mark m_2. Since the surface tension at the end of the capillary where the liquid emerges into the air exerts a back pressure which is different for different liquids and is difficult to determine, the average pressure h is not clearly defined by the dimensions of the instrument, and the application

[6] To avoid errors it should be noted that the values etched on the capillaries for k give ν in centistokes. If values in cm. and sec. are inserted in equation (2)—

$$k = 100\,\frac{\pi g h r^4}{8 l V}.$$

of equation (3) causes errors of several per cent.[7] In addition to this, the temperature is difficult to regulate, since the end of the outlet tube projects from the bottom of the bath, and the temperature of the test liquid must be freshly adjusted before every check test, since between tests the liquid is exposed to room temperature. In spite of this defect, this type of instrument is

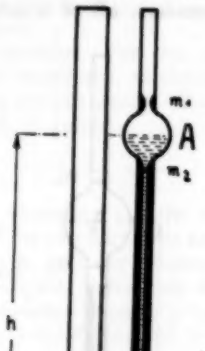

FIG. 2.
CLOSED VISCOMETER (OSTWALD'S DESIGN).

still used on account of its simplicity, just as are the fundamentally similar technical viscometers of Engler, Redwood and Saybolt, with which, however, the Hagenbach correction is often greater than the viscous resistance, so that they cannot be called capillary instruments.

(*c*) *Closed Instruments.*—The disadvantages of the pipette are avoided in other viscometers, the capillaries of which discharge

[7] Ronceray found errors in viscosity of 4 per cent. with glass capillaries. (*Ann. Chim. Phys.*, 1911, **22**, 107.)

not into the air, but into a lower bulb. With the apparatus of Ostwald [8] (Fig. 2), for example, an accurately measured volume of liquid is introduced into the lower bulb B and is drawn into the upper bulb A by applying suction to the smaller tube. Then the liquid is allowed to flow back under its own head and the time t is determined in which the meniscus falls from mark m_1 to mark m_2. In this case h is not affected by the surface tension,[9] and the equation—

$$\nu = t\,k$$

therefore holds rigidly on the assumption that the average pressure head h is equal for all liquids. As a rule, this assumption is complied with sufficiently if a constant volume of liquid is introduced into the instrument, as it is attempted to accomplish by various means.

By the use of a pipette, the fixed normal volume is definitely introduced. This method is satisfactory for liquids of low and nearly the same viscosity (for example, watery solutions), but for viscous liquids (for example, mineral oils of very different viscosities) the method fails because for the pipette to discharge the normal volume requires an unknown and different time for each viscosity.[10] In such cases it is better to adopt the second method, that of determining the specific gravity and weighing, which is ordinarily accurate enough if care is taken, but is very inconvenient. The third method, fundamentally the best, but unfortumately the most inconvenient one, is to set the lower meniscus at a fixed elevation by means of a scale and telescope. This method is certainly not applicable to dark oils, because the meniscus cannot be clearly seen.

With instruments of the Ostwald type, therefore, the difference in level is theoretically defined with accuracy, but practically it cannot always be fixed without error. The fact that the volume introduced is correct for only one temperature and must be corrected for any other has been especially emphasised by Bingham; for this inconvenient correction has often been neglected even in scientific work on the viscosity–temperature relation.

It is obvious that under these circumstances efforts would be made to facilitate the adjustment of the pressure head. Thus,

[8] Already in the year 1897 Arrhenius had used this viscometer at the suggestion of W. Ostwald in Ostwald's laboratory. (Private communication from Wa. Ostwald.) Apparently it was first described in "Hand-und Hilfsbuch zur Ausführung physikochemischer Messungen," by W. Ostwald, 1893, Leipzig, p. 195.

[9] Apart from the short periods of passage through m_1 and m_2, the surface tensions at A and B are small, because the diameter of the meniscus is large. With suitable form and size of bulbs, as is well known, this effect can be disregarded; cylindrical bulbs are more suitable than spherical bulbs.

[10] On account of the liquid clinging to the walls. See p. 413.

for example, Grüneisen[11] placed a sharp-pointed wire inside the lower bulb, by means of which the lower meniscus could more readily be adjusted. For the same purpose Bousfield[12] constructed a somewhat complicated instrument with constrictions and filling marks. The British Standard viscometer[13] also has special filling marks. Now it is true that the liquid level can be read accurately enough by the marks, but it takes considerable trouble, and auxiliary instruments are required to adjust the meniscus to a mark.

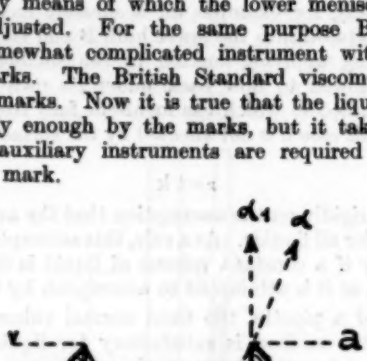

FIG. 3.
RESERVOIR WITH OVERFLOW.

(*d*) *Instruments with Overflow.*—Attempts are therefore made to adjust the filling height automatically. Martin[14] uses an overflow which had previously been used by Vogel[15] in the Vogel-Ossag viscometer (Fig. 3). However, the surface of the liquid does not adjust itself exactly to the level of the overflow rim, *a*, but is lower,[16] and, in fact, the level lies at a distance **x** below the rim, corresponding to the height the edge of the meniscus is raised at the solid wall. The height and form of the edge of the meniscus, however, are determined by the interfacial tension constants

[11] E. Grüneisen, *Wissenschaftliche Abhandl. der Phys. Techn. Reichsanstalt*, 1905, **4**, 151.
[12] Bousfield, *J. Chem. Soc.*, 1915, **107**, 1781.
[13] Standardised by the British Standards Institution.
[14] Martin, *Bull. Soc. Belg.*, 1925, **34**, 81.
[15] Vogel, *Zeitschr. f. angew. Chemie*, 1922, **35**, 561; also Saybolt and many others employ an overflow.
[16] When the hook mentioned by Erk is used; without this the adjustment is less certain. See note 18.

a and a_1, and by the specific gravity, and are different for every liquid.

In the flow over the overflow rim, therefore, surface tension, and with it the main error of the pipette instrument, returns and the result is that h is not accurately defined. Since, moreover, the Vogel-Ossag viscometer is built with interchangeable parts, and the necessary tolerances cause variations in the height of the marks m_1 and m_2 above the overflow rim, and in the working volume,[17] it is not surprising that even with mineral oils the instrument shows errors of ± 2 per cent. and higher,[18] that is, just as high as those of the technical instruments of Engler, Redwood, Saybolt, etc. If now we also take into consideration that an overflow corrects only for increasing but not for decreasing volumes, and thus is applicable only with constant or rising but not with falling temperatures, if we consider further that the force of gravity always acts against the flow over the overflow due to interfacial tension, and thus the small head x is developed very slowly, and lastly if we consider that capillary action—which occurs, for example, when the thermometer is too near the walls of the container—may have quite a strong effect to vitiate this adjustment, then, all things considered, the overflow appears to be a fundamentally unreliable means for our purpose.

(*e*) *General considerations of available viscometers*[19] are briefly as follows :—

With relative viscometers the chief difficulty lies in fixing the pressure head.

With the Ostwald instrument this adjustment is possible only with much work and time, and is not free from error when a variety of liquids are used.

The pressure head is not clearly defined with pipette instruments and instruments with an overflow, and with the latter it may be accidentally disturbed.

[17] The tolerances alone could cause variations in the pressure head and in viscosity determinations of 1 per cent.

[18] According to Erk, *Forsch. auf. dem Gebiete des Ingenieurwesens*, 1927, No. 288, the limit of error with mineral oils is ± 2 per cent. These oils, however, have very low and almost constant surface tensions. In the case of liquids with more variable surface tensions, the errors are therefore larger; they could be still greater in consequence of neglect of the kinetic energy correction (see page 400).

[19] The list of instruments might be supplemented by those operating with pressure regulators and other auxiliary apparatus. Ordinarily these do not come under consideration because too complicated. For further information, see the excellent book of Barr, "A Monograph of Viscometry," 1931, London, in which various such instruments are described; also "The Viscosity of Liquids," by Hatschek, and the German edition, "Die Viskosität der Flüssigkeiten," published by Theodor Steinkopff, 1929, Leipzig, in which the theory of friction is considered at greater length. See also Erk, note 18.

In all cases the sources of error are located at the lower level, and with no instrument is the necessary certainty directly assured by the conditions. The methods of improvement which are still possible, or have been applied, appear exhausted or have been carried to too fine a point; any attempt to improve them further is therefore not advisable.

Finally, it is not only the lack of instruments itself, but also the neglect of the kinetic energy correction which, as we shall see later, leads to unexpectedly high errors, especially with the much-used capillary viscometers.

II. The Suspended Level.

(*a*) *Theory.*

Summary.—In this section the phenomenon of the suspended level will be described. It is explained how a suspended layer of liquid is formed, and how it is brought about that its surface is flat and there is no trouble from surface tension. It is calculated that the layer has the same thickness with all liquids, and that the suspended level lies always at the same elevation no matter how dissimilar are the liquids used. Although fundamental for the new instrument, theoretical knowledge is not required for its use; for that purpose the directions in Chapter III. are sufficient.

To attempt to avoid the disadvantages of an overflow by revolving it through 180° and thus changing its horizontal surface to a suspended one; thus to turn the lower bulb upside down, appears at first sight not only impossible but absurd. Yet this led to an ideal solution of the problem and to a new physical aid, the "suspended level." As this is a clue for the understanding of all the following sections, it will be considered first.

1. *The suspended level in dynamic equilibrium. Within the field of application of the Poiseuille formula:—*

Formation of the Suspended Layer.—Fig. 4 shows that capillary 4 is enlarged to a circular surface *a* at the top of the tube C of large diameter. When liquid is discharged from capillary 4 it turns through a right angle at the lower end of the capillary, and spreading out radially, it follows the horizontal circular surface *a* to its edge. Then, bending through another right angle, it flows vertically down the wall e of the large tube C. We shall consider this phenomenon for the case of flow so slow that the kinetic energy can be neglected. Then the simple Poiseuille formula (2) applies, from which the volume discharged from the capillary becomes—

$$V = t\,\frac{\pi g h r^4}{8 l V} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The same volume V, after leaving the capillary, passes as a suspended layer over the circular surface, the liquid being held

by forces of adhesion and cohesion. At the angle w between *a* and e there is formed a ring-shaped collar which, in consequence of surface tension, seeks to collect liquid behind it; in the vertical layer e it acts against gravity, but this is not the case in the horizontal layer at *a*. Consequently flow takes place in the direction a–w–e, and in fact this is flow with free surface, so that, assuming laminar flow, there may be derived from Newton's hypothesis, the formula [20]—

$$V_1 = t\, d^3\, b\, g\, \frac{h_1}{3 l_1 V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where d is the thickness of the liquid layer, b its width, l_1 its length and h_1 the pressure head.

Since the liquid spreads from the centre to the periphery of the circular surface, the width b of the path of the liquid increases constantly as the edge is approached, and (taking r_a as the radius

FIG. 4.

FIG. 5.

of the circular surface *a* to distinguish it from the radius of the capillary r) then $b = 2 r_a \pi$. If this relation is inserted in equation (5) we have—

$$V_1 = t\, d^3\, 2 r_a \pi\, g\, \frac{h_1}{3 l_1 V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Thus d^3 decreases as r_a increases. If it is assumed as a first approximation that the velocity of flow is constant, the layer of

[20] The formulas for open channels, common in practical hydraulics, apply to turbulent flow and are not valid here.

liquid on the circular surface must be thinner at the edges than in the middle. This variation in thickness must have the result that the layer of liquid suspended under the circular surface tends to take the form of a disc generated by a curved line. The formation of such a shape, however, is opposed by surface tension, which tends to make the surface as level as possible. Both effects therefore, acting together, must determine the shape of the liquid surface. A test under conditions such as occur in viscosity measurements[21] gave the form of surface shown in Fig. 5. The pressure which the arched surface exerted in the direction of the capillary axis was considerable; it amounted to 2 mm. in a similar case with water, and since the back pressure depends on the surface tension and so will be different for different liquids, the arrangement was not yet serviceable for viscosity measurements.[22]

Formation of the Flat Surface.—Now it is possible to provide the space which the liquid needs and which it otherwise obtains by deformation of the surface. Space may be placed at its disposal by not leaving the circular surface flat as in Figs. 4 and 5, but hollowing it out in a funnel form. The generating curve for the funnel is found as follows.

Since on ground of continuity

$$V = V_1$$

it follows from equations (4) and (6) that

$$d^3 = \frac{r^4}{r_a} \frac{3}{16} \frac{h}{l} \frac{l_1}{h_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Introducing $r_a = \beta r$ and, for the sake of simplicity, letting

$$\sqrt[3]{\frac{3\,h\,l_1}{16\,l\,h_1}} = C_1$$

we have

$$d = r \sqrt[3]{\frac{1}{\beta}} \cdot C_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

[21] With a difference in level h of 125 mm. and with a diameter of capillary of 1 mm., the time of discharge of 5 cm.^{3} being about 40 sec.

[22] It is indeed hardly necessary to mention that it is not permissible to use the customary funnel form with S-shaped side surfaces for the transition between the capillary and the large tube. For liquid surfaces, concave to the air, would always form at the bent wall surfaces of the funnel, and the liquid surfaces would exert a pull in the direction of the capillary axis. Form and position of the concave surfaces, however, do not depend only on the form and diameter of the funnel, but also among others things on the specific gravity and the surface tension. One can calculate the form and find that the vertex of the concave surface lies lower with high surface tension, and has a larger radius of curvature, than with lower surface tension. Elevation and pull are therefore different for different liquids and therefore not suited to our purpose.

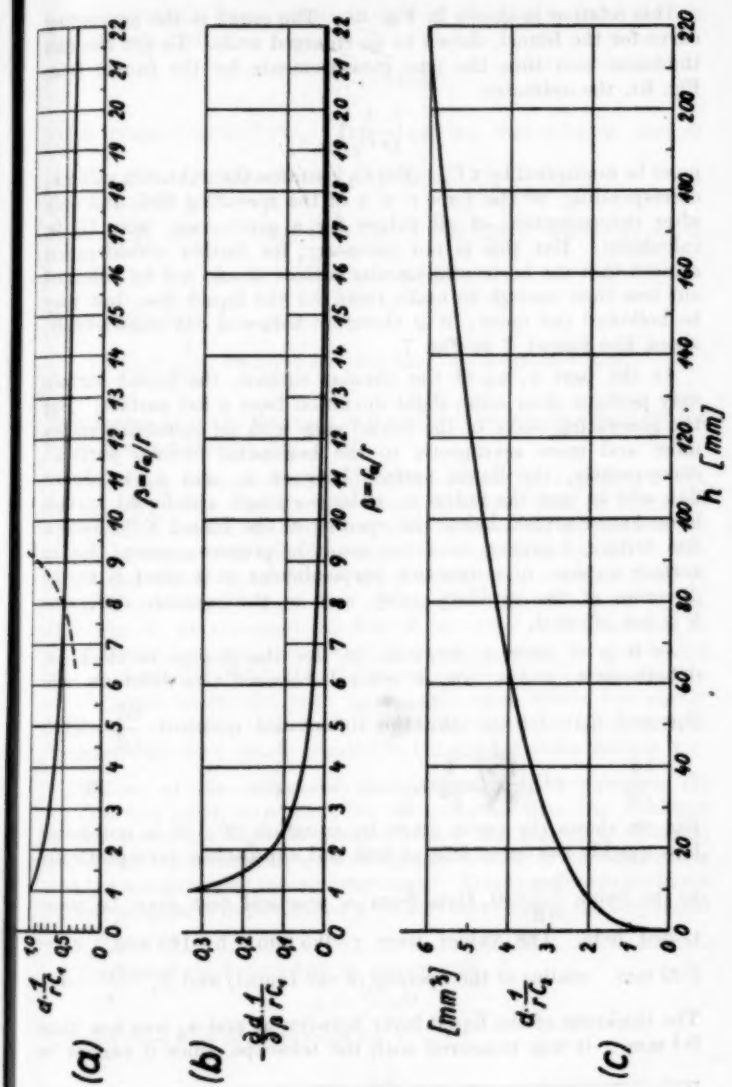

FIG. 6.

This relation is shown in Fig. 6A. The curve is the generating curve for the funnel, shown to an enlarged scale. To get the film thickness, and thus the true measurements for the funnel from Fig. 6A, the ordinates

$$\left(\frac{d}{r\,C_1}\right)$$

must be multiplied by $r\,C_1$. But C_1 contains the unknown value h_1 corresponding to the force e–w–a of the spreading film, and only after determination of all values for a given case, may C_1 be calculated. But this is not necessary, for further consideration showed that the horizontal circular surface should not be hollowed out less than enough to make room for the liquid disc, but may be hollowed out more; it is therefore hollowed out considerably, about like funnel T in Fig. 7.

At the part a_1–a_2 of the circular surface, the liquid surface may perhaps show some slight deviation from a flat surface. But the generating curve of the funnel runs with an increasing radius more and more asymptotic to the horizontal circular surface; consequently, the liquid surface between a_1 and a_2 is almost flat, and in case the radius r_{a1} is large enough, the liquid surface is no longer arched below the opening of the funnel T.[23] Such a flat surface, however, does not result in pressure action, due to surface tension, in a direction perpendicular to it (that is in the direction of the capillary axis), and so the pressure difference h is not affected.

As it is of interest, however, to test the change in thickness d between a_1 and a_2 (or, in general, between two different radii $\beta_1 r$ and $\beta_2 r$), let us take the differential quotient $\frac{\partial d}{\partial \beta}$. Then

$$\frac{\partial d}{\partial \beta} = -r\,C_1\,\frac{1}{3}\sqrt[3]{\frac{1}{\beta^4}} \qquad (9)$$

Fig. 6B shows the curve given by equation (9). It is noticeable how quickly the curve falls at first and approaches asymptotically to the value $\frac{\partial d}{\partial \beta} = 0$. Data from a practical test may be mentioned here. The values were $r = 0{\cdot}5$ mm., $h = 140$ mm., $r_{a1} = 2{\cdot}25$ mm. (radius of the opening of the funnel) and $\beta_1 = \frac{r_{a1}}{r} = 4{\cdot}5$. The thickness of the liquid layer between a_1 and a_2 was less than 0·1 mm.; it was measured with the telescope, since it cannot be

[23] That is, no longer arched to a noticeable degree.

calculated solely from equation (8). If Fig. 6A is entered with $\beta_1=4{\cdot}5$, we find

$$\frac{d}{r\,C_1}=0{\cdot}605,$$

which means $d=0{\cdot}605\,r\,C_1$. This d was less than 0·1 mm., and so

$$0{\cdot}605\,r\,C_1<0{\cdot}1 \text{ mm. or } r\,C_1<\frac{1}{6{\cdot}05}.$$

From Fig. 6B it may then be found that when $\beta_1=4{\cdot}5$,

$$\frac{\partial d}{\partial \beta}\frac{1}{r\,C_1}=0{\cdot}045.$$

If we introduce

$$r\,C_1<\frac{1}{6{\cdot}05}, \text{ we have for this case } -\frac{\partial d}{\partial \beta}<0{\cdot}0074 \text{ mm.}$$

That means that the decrease in d equalled or was less than 0·0074 times the increase in β.[24]

Thus, if by suitable form and dimensions of the capillary outlet the liquid surface under *a* can be so flattened that its effect on the pressure head h lies far below the experimental error, then the effect becomes still smaller from the following reason. The suspended liquid layer forms at the corner w, a collar (Fig. 7) concave downward, which also affects the suspended layer $a_1\,a_2$. If in Fig. 6A we represent the flow of the collar at w according to its direction, we get the dotted line which cuts the generating line of the liquid disk. If the dimensions are so selected, the two effects meet below the path $a_1\,a_2$, and their effects are partly balanced, with the result that the path $a_1\,a_2$ of the liquid surface becomes still more nearly parallel to the solid circular surface *a*.

Position of the suspended level.—Finally, from equation (7) we find the proof, important for our purpose, that the ***thickness of the suspended layer is independent of the kinematic viscosity, and so has the same value with all liquids***, so long as the dimensions and the pressure head remain unchanged. It is therefore superfluous for our purpose to determine at what elevation within the suspended

---

[24] One should really enter Figs. 6A and 6B with

$$\beta \sim \frac{\beta_1+\beta_2}{2}$$

and then get a more accurate value for

$$\frac{\Delta d}{\Delta \beta}$$

which is still smaller than that calculated from β_1.

layer the true suspended level actually lies,[25] that is the level which defines the difference in head h. For since the thickness of the suspended layer is the same for all liquids, the suspended level is, with the greatest probability, at the same elevation with all liquids and adjusts itself automatically with physical certainty. Even if the suspended level within the suspended layer should be at a different height with different liquids, there could indeed be only a little difference, and as the layer is less than 0·1 mm thick, there might be a difference of some 0·01%, or far less than the probable error in our measurements.

This conclusion, arrived at from pure hydrodynamic considerations, is practically unaffected by the fact that the fields of molecular force at the interface between the liquid and solid wall cause adhering layers of special physical characteristics, containing differently oriented molecules with different liquids. For in this layer it is a question of dimensions of molecular size[26] which thus lie outside the accuracy of measurement of our apparatus and therefore need not be considered for our purpose of viscometry.

If the suspended level is used as the lower level of a relative viscometer, which is to be calibrated with a liquid of known viscosity, the fixed position of the suspended level enters into the calibration constant. *The calibration constant and the viscosity determination are thus free from all errors* which, with other viscometers, are unavoidably connected with the adjustment of the lower level.[27] On this fundamental advantage rests both the superior accuracy of the instrument with suspended level and also the simplicity of its operation.

Relation to Pressure Head.—If we again consider equation (7), we see that d increases only as the cube root of h; for we have with $r_a = \beta r$:—

$$d = r \sqrt[3]{\frac{1}{\beta}\frac{3}{16}\frac{l_1}{lh_1}}\sqrt[3]{h}$$

or with :—

$$\sqrt[3]{\frac{1}{\beta}\frac{3}{16}\frac{l_1}{lh_1}} = C_2$$

$$d = r\ C_2 \sqrt[3]{h} \quad \text{(when h is variable)} \ldots\ldots\ldots\ (10)$$

This relation is shown in Fig. 6c. Also $\frac{\partial d}{\partial \beta}$ increases with the

[25] Which would be difficult to determine on account of the parabolic velocity distribution in the capillary and the change in direction of its lower end.

[26] See also note 30.

[27] Concerning this error, see notes 7, 17 and 18.

cube root of h. If the change in $\frac{\partial d}{\partial \beta}$ with increased pressure is not desired, that is if the surface is not to become less flat, then from equation (9) by inserting C_1 we have :—

$$\beta^4 = h \frac{r^3}{\left(-\frac{\partial d}{\partial \beta}\right)^3} \frac{1}{144} \frac{l_1}{l h_1} \quad \ldots\ldots\ldots\ldots\ldots (11)$$

Equation (11) may also be written :—

$$r_a = \sqrt[4]{h}\, r \sqrt[4]{\frac{r^3}{\left(-\frac{\partial d}{\partial \beta}\right)^3}} \sqrt[4]{\frac{1}{144} \frac{l_1}{l h_1}} \quad \ldots\ldots\ldots\ldots\ldots (12)$$

The radius of the opening of the funnel must therefore be changed in proportion to $\sqrt[4]{h}$. Otherwise the flow will not be affected, so that the instrument is also fundamentally applicable to use with an external source of pressure. (But see p. 411.)

The Suspended Level in the Regimes of the Hagenbach Correction and of Turbulence.

SUMMARY.—In this section it will be shown that the suspended surface is no longer flat at high velocities of flow, but is arched downward, but yet it acts as a large mass of liquid directly entered by a jet from the capillary.

We have been concerned till now only with the regime of the simple Poiseuille formula, where the energy of motion is so small that it can be neglected. But it is not only of theoretical interest but, as we shall see, it is of importance in practical viscometry to consider the regime of high velocities where the kinetic energy can no longer be neglected. In this regime, formula (2a) applies, which contains the Hagenbach term[28] for which, as for the simple Poiseuille equation, laminar flow is assumed. Its validity ceases when laminar flow ends, and this, as is well known, is followed by turbulent flow at still higher velocities. Since turbulence occurs the more readily the wider the container, it starts first at the mouthpiece of the capillary, but under certain circumstances it may extend into the capillary. With turbulence enter other resistances, expressed in terms of the square of the velocity, which, however, we shall not consider more closely because this regime does not come into consideration in practical viscometry.

If the capillary discharges, as in Ostwald's instrument, into a large volume of liquid, then, according to Erk,[29] the jet from the

[28] E. Hagenbach, *Pogg. Ann.*, 1860, **109**, 385; M. Couette, *Ann. de Chim. Phys.*, 1890, **21**, 433.
[29] Erk, see note 18.

capillary extends far into the mass of the liquid where the energy of motion is dissipated. With the suspended level, however, it is the surface which dissipates the energy of motion, it being arched elastically downward. If the velocity of discharge is increased, the arching takes the form of a plug, Fig. 8; if the velocity is further increased, vibration of the plug may be noted. With still further increase, the plug falls in drops and finally in a continuous stream from the suspended surface, which sometimes appears quiet and sometimes clearly flutters. At what time the simple arching of the surface will be disturbed by the other phenomena depends in the first place on the velocity, but also on such constants of the liquid as surface tension and specific gravity.

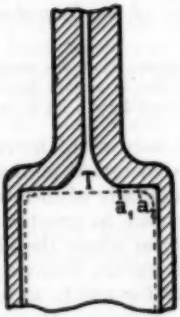

FIG. 7.

FIG. 8.

It may also be noted that there is a serious confusion in the literature in regard to the expressions "energy of motion" and "turbulence," which are used one for the other and almost always incorrectly. Doubt is expressed whether the kinetic energy correction is at all necessary, and, as we shall see, it is generally neglected. In papers whose whole basis rests on hundreds and thousands of viscosity determinations, not only is the correction neglected, but not even are the dimensions r l h and V given, so that it is not possible to apply the correction afterwards. The case of the Vogel-Ossag instrument, previously described, can cause no surprise; it is not at all a unique case.

For our subject it was to be determined whether the suspended level in the regime of the Hagenbach correction—that is, when the surface is deformed (but yet broken through) by kinetic energy—still acts like a large mass of liquid which the jet enters, as, for example, with the Ostwald viscometer (Fig. 2). The theoretical result of the previous section makes that possible, and comparable tests with the suspended level and ordinary liquid surfaces, which are described on this page, proved it conclusively. Therefore further theoretical treatment was dispensed with, which, moreover, would have encountered many difficulties.

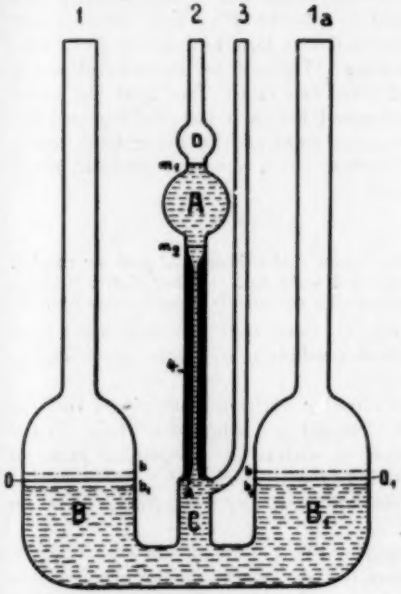

FIG. 9.
ORDINARY LIQUID SURFACES.

FIG. 9A.
SUSPENDED LEVEL.

SPECIAL APPARATUS TO TEST THE THEORETICAL CONCLUSIONS (3/10 SIZE).

2. *The Suspended Level in Static Equilibrium.*

SUMMARY.—In this section it will be shown that the suspended level is a true level surface and coincides with the surface of the suspended layer.

If for any reason the flow from the capillary over the horizontal circular surface decreases in velocity, then since the force of gravity

at e (Fig. 4) remains active, the liquid layer below the solid circular surface becomes thinner, and if the flow stops entirely, it must finally become so thin that the particles of liquid are held by the molecular fields of force; it is then only a few μ thick and the flow stops.[30] Then since at the end of the capillary there is no longer any vertically acting pressure due to flow, the surface *a* remains flat and without exerting any pressure in the direction of the axis of the capillary. The suspended level lies then at the solid surface.

This is the limiting case when the suspended level is used to determine the capillarity constant according to the capillary rise method (see also p. 415), and it is noteworthy that the capillary rise does not change for hours if the liquid does not evaporate and is not disturbed by shaking. The not to be underestimated advantage of the suspended level lies in the fact that the lower level does not need to be adjusted for each test, for in measurements of capillary rise the adjustment of the lower level meets with exactly the same difficulties as in viscosity measurements with the Ostwald instrument.

(*b*) *Experimental Part.*

SUMMARY.—In this section the results of the theoretical part are checked by comparative tests with suspended level and ordinary liquid surfaces, and also facts are established concerning the kinetic energy correction.

The object of the tests was to show that the suspended level really occurs at the elevation predicted and acts according to theory, so that:—

1. It lies below the solid circular surface, both when there is flow in the suspended layer of liquid and when it is still. In the first case the suspended level is within the suspended layer of liquid, and in the second case it lies at its surface.

2. The suspended level does not exert any force in the direction of the axis of the capillary.

This was proved by comparing the action of suspended levels, on the one hand, and ordinary liquid surfaces on the other, in the same apparatus, and the action was found to be the same in static and dynamic equilibrium and in the turbulent regime.

1. *Tests in Dynamic Equilibrium.*—Apparatus and method of operation.

With Ordinary Liquid Surface.—To make the tests, use was made of the special apparatus shown in Fig. 9, which made it possible

[30] The thickness of the film held by molecular fields of force is inadequately known, but on its type and thickness depends the lubrication in the so-called regime of semi-dry friction. (See, for example, Lederer, Mitteil. d. I.P.K., *Petr. Z.*, 1932, **28**, No. 49, 6.) I shall shortly show a method for measuring film thickness.

to obtain alternately a suspended level or an ordinary liquid surface at the same height, and thus to get the best imaginable means of comparison. To the bulb A, with the two marks m_1 and m_2, is attached capillary 4, which expands into the circular surface *a* in the large tube C. This tube branches and thus forms a connection with the two[31] bulbs B and B_1. These bulbs are open to the atmosphere through tubes 1 and 1a, and tube C opens through the smaller tube 3. The bulbs B and B_1 carry the marks O and O_1 at the same elevation as the horizontal circular surface *a*.[32]

Now enough liquid is introduced so that when the liquid is drawn up to mark m_2[33] the menisci in the bulbs B and B_1 will be just as high above the plane O a O_1 as it lies below this plane when bulb A is completely filled to mark m_1. Then the time of fall of the meniscus from m_1 to m_2 is measured. Since at the same time the lower level passed through the short path b b_1 symmetrical to the average level O a O_1 the effect was the same as if the level had been kept constant at O a O_1. The times of flow found in this way gave completely concordant values, so long as one and the same filling was used. Each time, however, that the instrument was freshly filled, there were slight deviations, even with the most careful work (col. 6 of the table), which may be explained from the fact that even with telescope and scale (the most accurate method previously known) it was not possible to adjust to the same filling height.[34]

With the Suspended Level.—Alternating with the just described tests with the ordinary liquid surface, tests were made with the

[31] Two bulbs were used only to eliminate the effect of small deviations from the horizontal in experiments with ordinary liquid surfaces.

With the suspended level it makes no difference whether the solid circular surface is horizontal or slightly inclined. Shaking strongly enough to cause regular waves over the circular surface has hardly any effect because the following liquid immediately makes up any deficiency that arises.

[32] It is seldom possible to get the two marks in the same plane; auxiliary marks are used, upon which the crosshairs of the telescope are set.

[33] Tube 3 must now be closed by the finger, as otherwise air passes from it into tube C.

[34] The height cannot be better adjusted than by emptying the contents of a pipette into the instrument. A pipette discharges equal volumes with liquids of about the same viscosity, but not when the liquids are of very different viscosity and surface tension, as is the case, for example, with mineral oils. This is shown by the data (given later, p. 413) concerning the liquid hanging to walls of bulbs. The adjustment, however, can be facilitated with the help of the results of the next chapter. For it is shown there that the capillary rise is the same for the suspended level and the ordinary liquid surface. Therefore the crosshairs may be set, not on the large meniscus—which is somewhat inconvenient—but on the meniscus in the capillary, and thus work can be done not only more conveniently but also somewhat more accuractely, without to be sure attaining the most reproducible results as with the suspended level.

suspended level. In fact the alternation was carried out so that the tests would be influenced as little as possible by the temperature variations that are unavoidable in a long series of tests. To establish the suspended level, the two tubes 1 and 1a were connected by rubber tubes with a large flask in which a vacuum could be maintained. Then first tube 3 was closed and by suction at 2 the liquid was drawn up to above the mark m_1. Then a slight vacuum was produced in the flask, and thus in the bulbs B and B_1 connected with it, which had the effect that air entered through 3, after tube 3 was opened. The entering air caused the liquid in C to break away, and thus the suspended level is formed at *a* (or rather a few hundredths of a millimeter below *a*). This phase of the test is shown in Fig. 9A. The flow test with suspended level[35] is begun by opening tube 2.

Results of tests with both types of lower levels. Since the viscosities of the liquids tested varied greatly, three instruments were used with capillaries of different diameter (see col. 1 of Table I.).

Column 7 contains the average value of the time of flow with ordinary liquid surfaces, and col. 9 those with the suspended level. The differences between the two never amount to more than 0·1 per cent., and are probably due to unavoidable errors in measurement of temperature and time. Each time, however, that the filling was changed, tests with the ordinary liquid surface gave somewhat different values, because in spite of the greatest care with telescope and scale it was not always possible to set the same level in the bulbs B and B_1. However these deviations (col. 6) generally[36] do not exceed 0·2 per cent. and correspond to the assumed error of $\pm$ 0·1 mm. in adjusting the level of the liquid surface. It may also be especially pointed out that this variation appears only with the ordinary liquid surface and not with the suspended level, with which the time of flow remained unchanged also after refilling. Such a result was also to be expected, for it is in agreement with the theory according to which the suspended level must be entirely independent of the volume of liquid in B and B_1. The theory makes the same demand in regard to the specific gravity and other constants of the liquid, and it is confirmed by the tests, for even wide variations in gravity (0·887 to 2·960, col. 4) and varying surface tension (α=2·2 to 7·8, col. 5) remain without effect.

[35] The tests with the suspended level and the ordinary liquid surface are only directly comparable if there is no disturbing hydrodynamic resistance to flow between the circular surface *a* and the surfaces B and B_1. Thus, such tests could not be made with the instrument of Fig. 10, since its tube g is too narrow.

[36] They are greater only in lines 9 and 10; here, however, this is due to the short time of flow and turbulence.

TABLE I.

1 Number and nominal dimensions of Capillaries.	2 Liquid.	3 Temperature. °C.	4 Density. ρ	5 Surface tension against air. α	6 Observed time of flow in sec., with special instrument of Fig. 9. With ordinary level. Average after each refilling.	7 Average of all tests.	8 Observed time of flow in sec. with special instrument of Fig. 9. With suspended level. Average after each refilling.	9 Average of all tests.	10 Hagenbach correction in a. Sec.	b. %.	11 Corrected time of flow in sec. Col. 9 minus Col. 10a.	12 Relative value of the capillaries.	13 Col. 12 is calculated from Col. 11 and in fact from the lines indicated below.	14 Kinematic viscosity ν in centistokes.
	1 Gasoline	21·5	0·7508	2·4	{90·9 91·1 91·3}	91·1	{91·0 91·1 91·2}	91·1	3·55	3·9	87·55		(12·06)	1 : 9	0·6539
I.	2 Benzole (impure)	21·8	0·8762		{95·4 95·9}	95·7	{95·6 95·8}	95·7	3·38	3·54	92·32		(12·07)	2 : 10	0·6895
r = 0·3 mm. l .. 100 mm. h = 130 mm. V = 5·429 cm³ k_I = 0·007469	3 Water	20·0	0·9982	7·2—7·8	{136·9 137·1 137·2}	137·1	{137·1 137·1 137·1}	137·1	2·36	1·72	134·74				1·0064 §
	4 Denatured ethyl-alcohol.	21·4	0·8128	2·2	224·4	224·4	224·6	224·6	1·44	0·64	233·16	I : II	(11·86)	4 : 11	1·6668
	5 Acetylene tetra-bromide.	19·9	2·960		{490·0 490·3 491·0}	490·4	{490·7 490·9 491·0}	490·6	0·66	0·15	489·94		11·64	5 : 12	3·659
	6 Aniline	20·0	1·014		571·0	571·0	571·2	571·2	0·57	0·10	570·63		11·67	6 : 13	4·262
	7 Amyl alcohol ..	21·9	0·8156		{691·0 692·1}	691·6	{691·6 691·9}	691·8	0·47	0·068	691·33		11·64	7 : 14	5·164
	8 Mineral oil No. 1	20·0	0·8871	3·0—3·1	1528·0	1528·0	1529·0	1529·0	0·21	0·014	1528·79		11·67	8 : 15	11·419
	9 Gasoline	21·5	0·7508	2·4	{10·2 10·1 10·3}	10·2	{10·2 10·2 10·2}	10·2	2·94	28·8	7·26				
	10 Benzole (impure)	21·8	0·8762		{10·3 10·6}	10·5	{10·4 10·6}	10·5	2·85	27·2	7·65				
II.	11 Denatured ethyl-alcohol.	21·4	0·8128	2·2	20·3	20·3	20·3	20·3	1·48	7·3	18·82				
r = 0·565 mm l = 100 mm. h = 130 mm. V = 5·856 cm³ k_{II} = 0·08714	12 Acetylenetetra-bromide.	19·9	2·960		{42·6 42·9}	42·8	{42·8 42·8}	42·8	0·70	1·6	42·1				3·669
	13 Aniline	20·0	1·014		49·5	49·5	49·5	49·5	0·60	1·2	48·9				4·261
	14 Amyl alcohol ..	21·9	0·8156		{59·8 59·9 60·0}	59·9	{59·9 60·0 59·9}	59·9	0·50	0·83	59·4				5·176
	15 Mineral oil No. 1	20·0	0·8871	3·0—3·1	131·1	131·1	131·2	131·2	0·23	0·18	130·97				11·41
	16 Mineral oil No. 3	20·0	0·8908	3·0—3·1	1752·0	1752·0	1750·0 1750·1	1750·0	0·017	0·001	1749·98	II : III	10·76	16 : 18	152·5
III.	17 Mineral oil No. 2	20·4	0·8899		150·2	150·2	150·1	150·1	0·017	0·01	150·08				140·8
r = 1·0 mm. l = 100 mm. h = 130 mm. V = 5·333 cm³ k_{III} = 0·938	18 Mineral oil No. 3	20·0	0·8909	3·0—3·1	{162·6 162·7}	162·6	{162·6 162·6}	162·6	0·016	0·01	162·58				152·5

§ This value was used as the basis of calculations of ν; according to the opinion of Bingham and Jackson (Scientific Paper No. 298 of the Bureau of Standards, 1917) and others it is the most reliable.

The correction for kinetic energy (col. 10) in lines 8 and 16 to 18 is less than 0·02 per cent., and it can therefore be neglected. In other lines the correction is at times considerably greater and in line 9 reaches a value of 28·8 per cent. Accordingly the suspended level shows the special phenomena already described on p. 392, arching is clearly shown, and with benzole the suspended surface fluttered. And yet there was never any difference between the time of flow with the ordinary liquid surface and with the suspended level. That shows that not only in the regime of the simple Poiseuille formula (2), but also in that of the Hagenbach correction, —yes, even in the turbulent regime—the suspended level and the ordinary liquid surface act in accord, which furnishes the experimental proof for the requirements of the theory set up in the theoretical part of this paper.

Moreover, further very important conclusions for viscometry may be drawn from our tests. For if we subtract the correction in seconds in col. 10 (*a*) from the observed time of flow in col. 9, we get the corrected time of flow of col. 11. If from this we get the relative values for capillaries I. : II. and II. : III., we have the values of col. 12. Except for the bracketed values, these agree very well, for the variations do not exceed 0·2 per cent. Since the time of flow for capillary II. in line 12 is only 42·8 sec., and is only 49·5 sec. in line 13, with such short times the 0·2 per cent. limit of our watch of itself makes an error of 0·4 per cent., so that the variation of the relative value in lines 5 to 8 is not greater than the expected error in time.

The agreement of the ratios in brackets is not so good. The reason for this is easy to see; it is due to the fact that for the short times of flow with capillary II. (lines 9 to 11) the Hagenbach correction is too uncertain. The negative Hagenbach term of equation (2*a*) is known to be somewhat too large, since with a time of flow of about 17 seconds in capillary I. it would be as large as the first term in equation (2*a*), larger than it could ever be if it were a correct expression for the correction. For the special purpose of the table of corrections on p. 409 the formula should be checked, especially regarding m and the Couette[36] correction for conditions at the ends of the capillary.

Finally, the tests have consequences and suggested points of view which do not belong to our proper subject, but deserve at least to be mentioned. First, the old controversy,[37] whether the kinetic energy correction must be applied or not when the liquid flows from a capillary into a large volume of liquid, is answered affirmatively; for it is now clear that the suspended liquid surface exerts a back pressure when arched by the energy of motion,

[37] Erk, *loc. cit.*

and since the suspended surface and ordinary liquid surfaces give the same results even with highest kinetic energy corrections, any other conclusion is not at all possible.

Other questions, for example, that of the propagation of turbulence phenomena from the ends to within a capillary, might also be readily studied in the above manner or by boring the capillary at several places as shown in Fig. 18. Also, lack of concordance in published papers concerning the phenomena in ends of capillaries might be explained by our clear method of comparison, in one and the same instrument, working alternately with suspended level and with ordinary liquid surfaces. To pursue all these matters further would lead us beyond the goal of the present paper.

2. *Tests in Static Equilibrium.*

According to the theory discussed on p. 393, in capillary rise determinations the suspended level must lie quite close to the circular surface, as is proved by the following experiment.

An instrument similar to Fig. 9 was used, which differed from it only in having a longer and smaller capillary (radius about 0·15 mm) and a millimeter scale starting from 0 at the circular surface *a*, as shown in Fig. 17. After the instrument was filled to exactly the height of the solid circular surface (O a O_1), tests were made alternately with the suspended level and the ordinary liquid surface, as described in the previous section. It was found that the average value of the capillary rise agreed in both cases, again with close agreement of check tests with the suspended level, as compared with slight variations observed after each refilling in tests with ordinary liquid surfaces. Therefore here, also, there is the same superiority of the suspended level as in the dynamic tests.

(*c*) Summary of results thus far presented.

The most important theoretically deduced and experimentally found results are as follows :—

1. If a vertical capillary as shown in Fig. 7 is expanded into a large tube, and liquid passes from the capillary into the tube, a suspended liquid layer is formed at the place of transition.

2. If the velocity of flow lies within the limits of application of the Poiseuille law, then the suspended surface is practically flat and exerts no back pressure in the direction of the capillary axis. The suspended level then lies within the suspended layer.

3. With one and the same apparatus and the same pressure head, the suspended layer is of equal thickness with all liquids. In the layer the suspended level is always at the same elevation. The thickness of the layer and the elevation of the suspended level are therefore completely (but compare p. 389) independent of the viscosity, surface tension and specific gravity.

4. At high velocities which are in the regime of the Hagenbach correction, the suspended surface is deformed; the suspended level, "however, has an effect just as if the liquid is going through a large volume of liquid to an ordinary Ostwald-level at the same elevation."

5. Also, when there is no flow, the suspended surface is level, and exerts no effect of pull or push in the direction of the capillary axis. The suspended level lies then within the suspended surface.

6. In the instruments with suspended level the head h is clearly defined, both in dynamic and in static equilibrium, for relative measurements, and adjusts itself automatically with physical certainty.

7. The suspended level is the simplest and most certain means for adjusting a hydrostatic pressure of this kind.

III. Practical Applications of the Suspended Level.

Summary.—In this section new instruments are described, which were built on the basis of the information obtained in Chapter II. They make use of the suspended level and a device for producing it at will. New dimensioning of the viscometer makes it possible to apply the kinetic energy correction by means of a table, and to obtain the kinematic viscosity without calculation.

Synopsis.—After it had been recognized what a fundamental advantage the suspended level had for adjusting the pressure head, it was applied to the following types of instruments:—

1. Viscometer for direct determination of the kinematic viscosity.
2. Viscometer for direct determination of the dynamic viscosity.
3. Pressure regulator.
4. Instrument for measuring capillarity constants.
5. Instrument for measuring dynamic surface tension.

These devices, which by no means exhaust the possibilities, will be discussed.

1. *The New Viscometer for the Determination of Kinematic Viscosity.*

(*a*) General (dimensioning to avoid calculations).

Error Due to Neglect of Kinetic Energy.—Before we consider the new viscometer more closely, we must take up again the kinetic energy correction already discussed on p. 398. Col. 10b of Table I. shows that with short times of flow the correction is so large that its neglect makes the test illusory. Yet this correction is often neglected, for example, with the Vogel-Ossag viscometer which has three capillaries very similar to ours.[38] If this apparatus

[38] The three capillaries of the Vogel Ossag had, for example, the constants k = 0·0113 and 0·197 and 1·16 with about the same values of r, l and h/V.

is used down to a time of flow of 25 seconds, according to the directions, there is with the smallest capillary I. an error of 50 per cent.[39], with the middle capillary II. one of 3 per cent., and with the largest capillary III. one of 0·6 per cent. This is certainly a very noteworthy circumstance with a widely used instrument whose good agreement in check tests appears until now to have been taken as a proof of the absolute correctness of the results. For in the numerous publications concerning this instrument, both in and outside of Germany, no mention has been made of a correction.

The Elimination of Errors.—Now a correction for kinetic energy can only be applied if the dimensions of the capillary are accurately known, which is difficult of itself, and besides one must use the inconvenient equation (2*a*) in calculation, so that success can not be obtained without a knowledge of hydrodynamics and without fine physical tools. It appeared most urgent to bring help here, and it was found to be possible. If we consider again the correction term of equation (2*a*), we see that all symbols except t and the factor m are instrumental constants. For a given apparatus the term may be tabulated as a function of t, so that the correction in seconds is given by multiplying by $\frac{1}{k}$. Now since with instruments of the same dimensions such a correction table would be valid for every instrument, all our instruments are made concordant by a special procedure.[40]

Going a step further, the instruments were so dimensioned that their calibration constants are only powers of 10 : for capillary I.=0·01, for capillary II.=0·1, for capillary III.=1. Then it is only necessary to subtract from the time of flow in seconds the correction in seconds taken from the table, and to multiply the corrected time with the appropriate power of 1 (*i.e.*, merely insert the decimal point) in order to get the kinematic viscosity ν in centistokes (cSt). The correction table[41] for our apparatus is given on p. 409.

By this kind of dimensioning and the correction table, the instrument has been freed from calculations in use. Since in

[39] For mineral oils for which the viscometer is primarily built, the errors are not so large but are yet not negligible. With a naphtha of 0·66 cSt, which has a time of about 85 sec. in capillary 1, the error amounts to about 5 per cent. ; with a mineral oil of 5 cSt (1·4 Engler degrees), with a time of flow of 25 sec. in capillary II., the error is about 2·4 per cent. There are, in addition, the errors previously referred to (notes 17 and 18).

[40] We must abstain from a more accurate description.

[41] The values might be changed after the revision of calculations by equation (2a), referred to on p. 378. The revised table will then appear in the " Internationale Tabellen für Viscometer " (see note 48).

consequence of the suspended level it is also suited for previously unattainable accuracy, there should be in the future no longer any excuse for faulty viscosity data.

Calculation of the Correction Table on p. 409. Diameter of the Capillary and the Required Volume V.—For all our capillaries the length is taken as $l = 90$ mm, and the average pressure head $h = 130$ mm. for constructive reasons. Starting from a radius of $r = 0{\cdot}565$ mm. for capillary II., whose calibration constant is to be $k = 0{\cdot}1$, the required volume is calculated by the equation :—

$$V = \frac{\pi\, g\, h\, r^4}{8\, l\, k} \cdot 100 \qquad \ldots\ldots (14)$$

$$V = \frac{\pi\ 981\ .\ 13\ .\ 0{\cdot}0565^4}{8\ .\ 9\ .\ 0{\cdot}1} \cdot 100 = 5{\cdot}6705\ \text{cm}^3.$$

If V has the same value for all capillaries, the radii r must vary according to $\sqrt[4]{k}$. Thus capillary I. with $k = 0{\cdot}01$ must have a radius of $r = 0{\cdot}565\ \sqrt[4]{0{\cdot}1} = 0{\cdot}565 : 1{\cdot}778281 = 0{\cdot}3177$ mm. For capillary II. with $k = 1{\cdot}0$, $r = 0{\cdot}565\ \sqrt[4]{10} = 1{\cdot}0047$ mm.

Calculation of the Corrections.—By combining constants, equation (2*a*) may be written :—

$$\nu = t\,k - \frac{k_1}{t} \text{ or } \nu = k\left(t - \frac{k_1}{k\,t}\right) \qquad \ldots\ldots (15)$$

That is to say there is to be subtracted $\frac{k_1}{k\,t}$ seconds from the time of flow t seconds. Various values are given in the literature for the coefficient m but $m = 1{\cdot}12$ is most generally used. Then in our case—*i.e.*, for all three capillaries :—

$$k_1 = \frac{m\,V}{8\,\pi\,l}\ 100 = \frac{1{\cdot}12\ .\ 5{\cdot}6705}{8\quad\pi\quad 9}\ 100 = 2{\cdot}80775.$$

Thus the correction to be applied is :—

$$\theta = \frac{2{\cdot}80775}{k\,t} \text{ sec.}$$

Or for capillary I. $\theta = \dfrac{280{\cdot}775}{t}$

for capillary II. $\theta = \dfrac{28{\cdot}0775}{t}$

for capillary III. $\theta = \dfrac{2{\cdot}80775}{t}$

The table on p. 409 has been calculated from these values.

(*b*) Details of construction.

The Three Capillaries.—The suspended level and a device to produce it at will, as well as the above described dimensioning to avoid all calculations, form the three new fundamentals of the apparatus which will be described in what follows only so far as necessary for use.

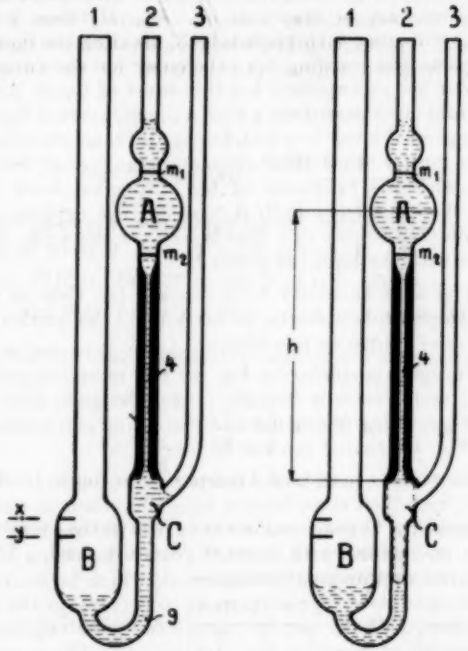

FIG. 10. FIG. 10A.

SCHEME OF APPLICATION OF THE SUSPENDED LEVEL TO A VISCOMETER. (3/10 SIZE).

To the pipette-like bulb A with marks m_1 and m_2 is attached the capillary 4 ending in a bulb C about 12 mm. in diameter. The end of the capillary is at the middle of a horizontal circular surface *a* at right angles to the capillary axis, as described more in detail in the theoretical part. Following the bulb C is a bent tube g and then the lower bulb B. This is connected with the atmosphere by tube 1 of large diameter, while C is connected

with the atmosphere through tube 3, the air inlet tube on "regulating tube."

If the bulb B has been filled through tube 1 until the meniscus lies between the marks x and y, and suction is applied to tube 2 through a rubber tube, closing tube 3 at the same time with the finger, then bulb C, capillary 4 and bulb A are filled in turn, so that conditions are as shown in Fig. 10. If tubes 3 and 2 are opened, air will enter C through tube 3, dividing the liquid at once into two parts and bringing it to the condition shown in Fig. 10A. At the lower end of capillary 4 a thin layer of liquid is formed on the horizontal circular surface *a* with a plane inverted liquid surface —the "suspended level"—which lies at the same elevation with all liquids, no matter what their characteristics (see p. 389). Simultaneously with the formation of the suspended level, the liquid begins to flow out from bulb A through the capillary. It does not fill bulb C but flows in a thin layer over the walls of this bulb and unites with the liquid in g and B.

Then it is only necessary to determine the time in which the meniscus passes from mark m_1 to mark m_2; this method of operation is thus as simple as possible.

The form used is similar to Fig. 10 but more compact, because tubes 1, 2 and 3 form a triangle. Also the glass body is placed in a frame consisting of circular end pieces and three rods, and is so inclosed (Fig. 11) that it can not be hit.[43]

The thermostat (constant temperature bath). The three capillaries, with their three frames, hang in a common bath (Fig. 12) that consists of a bottom and cover of cast bronze and a casing of Jena glass, and is filled with water.[44] Since the casing is cylindrical the capillaries appear greatly magnified, which facilitates reading. The upper base plate is pivoted so as to revolve on the lower base plate, so that the bath can be turned and each capillary brought into a convenient position for observation. The heating is not

---

[43] Thus the apparatus is less breakable than, for example, the usual Ostwald instrument or the glass capillaries of the Vogel Ossag, which are exposed to danger when a change is made from one to another.

[44] The constant temperature bath is filled with distilled water, which has first been boiled and then cooled, so that the air bubbles which otherwise would develop on first heating the bath will not cause trouble. Bubbles which, nevertheless, occur will vanish if the frame is lifted from the bath for a moment. If distilled water is not available, tap water is boiled, cooled and filtered, to avoid the otherwise bothersome separation of boiler scale. Development of micro fauna and flora, which may easily make the water in baths turbid on standing, may be avoided by the addition of 0·1 per cent. Raschit. ("Chem Fabrik von Dr. F. Raschig, Ludwigshafen a. Rhein.")

disturbed by turning, because the gas pipe to the Bunsen burner passes through the fixed bed plate. To cool below room temperature, a cooling coil may be inserted in place of one of the three frames. An air stirrer with rubber bulb completes the installation.

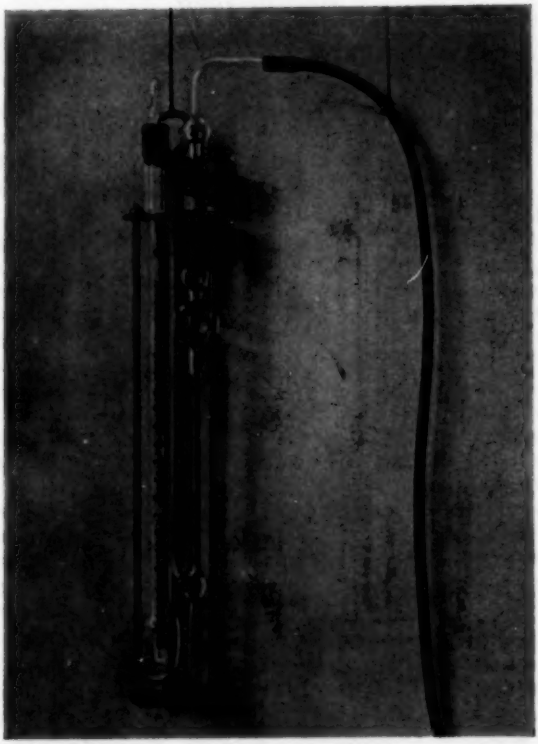

FIG. 11.

VIEW OF VISCOMETER WITH SUSPENDED LEVEL.

The instrument can be transported without packing, in the case (Fig. 12); also the three viscometers hanging in it do not need to be packed, for a spring plate in the upper part of the case exerts an elastic pressure and holds them fast in their normal position.

(*c*) Directions for use.

Carrying Out the Tests.—First, a preliminary test is made with the auxiliary pipette, in case it is not known which of the three capillaries of different diameter must be selected. For this purpose the liquid is drawn up to the mark on the bulb and allowed to flow

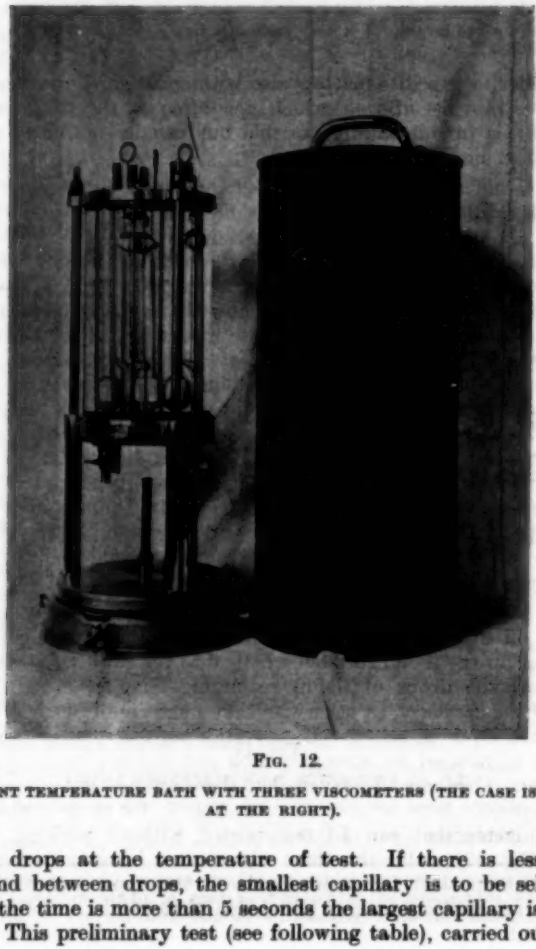

FIG. 12.

CONSTANT TEMPERATURE BATH WITH THREE VISCOMETERS (THE CASE IS SHOWN AT THE RIGHT).

out in drops at the temperature of test. If there is less than 1 second between drops, the smallest capillary is to be selected, and if the time is more than 5 seconds the largest capillary is to be used. This preliminary test (see following table), carried out in a

few seconds, prevents loss of time by selecting an unsuitable capillary:—

Calibration constant of capillary.	Field of application.	Preliminary test with auxiliary pipette.[45]
I. $k = 0{\cdot}01$ for the smallest capillary.	For all watery liquids, very thin oils and at high temperatures.	Drops fall at intervals of less than 1 sec.
II. $k = 0{\cdot}1$ for the middle capillary.	For most oils at 20° to 50° C.	Drops fall at intervals of between 1 and 5 sec.
III. $k = 1$ for the largest capillary.	For very viscous liquids.	Drops fall at intervals of more than 5 sec.

In order to expedite matters also with small capillaries, external pressures may be utilized, which, according to the considerations of p. 391, is fundamentally possible but usually not to be recommended in practice.

The liquid to be tested is poured into the selected instrument through the large tube 1 until the meniscus lies between the two marks, about 5 mm. apart; more accurate filling is not necessary. Then the instrument is lowered into the bath and the thermometer is inserted in tube 1. As soon as this thermometer and the other one which is directly in the bath show the same temperature, the test can be begun. For this purpose the rubber tube 13 (Fig. 11), by means of a suitable adapter, is attached to the upper conical end of tube 2, tube 3 is closed by the finger, and, by suction applied to the rubber tube, the liquid is drawn up until all three bulbs —C, A and D—are filled. No oil enters tube 3 and no air escapes from it. If the rubber tube is removed and directly afterwards—not previously[46]—the finger is raised from 3, air under atmospheric pressure enters bulb C through 3 and forms the suspended level as shown in Fig. 10A. At the same time the liquid flows out under gravity. The time t in seconds is measured in which the meniscus falls from the mark m_1 to the mark m_2.

The test can be repeated immediately as soon as the finger is placed on tube 3 and the oil again raised. It is advisable before drawing up the liquid to blow a little into the rubber tube in order to expel the drops of liquid remaining clinging in the lowest part of the capillary, as otherwise they might easily form a bubble when the liquid is raised. If, nevertheless, a bubble is formed, it can be eliminated by strong suction and sudden breaking of the vacuum. Care must be taken that there are no air bubbles below the suspended level or in the funnel (Fig. 7), for these might somewhat increase the time of flow.

[45] The number of drops is determined for mineral oils; it is influenced by the surface tension, which is nearly constant for all mineral oils. A higher surface tension somewhat decreases the number of drops.

[46] Not before, because otherwise air can rise up through the capillary.

Reading the Temperature.—Since the viscosity of many materials varies very greatly with the temperature, the test should not be begun until both thermometers agree exactly. Oils are bad conductors of heat, and it can take a surprisingly long time until they reach the temperature of the bath. This fact is taken into account in making it possible to hang three capillary instruments in the bath at one time; while two of them are coming to temperature, the third is being used. The time of waiting, however, may also be greatly shortened by at times moving the liquid back and forth.

Since the thermometers do not project from the bath, the burdensome and seldom entirely reliable correction for "emergent stem" is not necessary.

It is relatively easy to bring the thermometers to the same reading, but, on the other hand, very difficult to accomplish this at a pre-determined temperature, for example, 50° C. For practical purposes it is therefore to be recommended to measure the viscosity at any temperature near the desired temperature, and then, with the help of the temperature co-efficient of viscosity, calculate the viscosity at exactly 50° C. Graphical methods which greatly simplify such determinations are given in the International Viscometer Tables referred to later.

Reading off the Results.—In the first column of the correction table, the time in seconds is sought which is nearest to the observed time, and in the same line, in the column for the particular capillary used (I., II. or III.) the correction in seconds may be found. This correction is subtracted from the observed time of flow in seconds.[47] The corrected time in seconds thus obtained is multiplied by the factor k etched on each instrument, and, as this is always a power of 10, it is only necessary to insert the decimal point in the corrected time in seconds, to obtain the kinematic viscosity ν in centistokes (cSt):—

Example:

Observed time of flow from capillary I.	175·6 sec.
Correction taken from table	1·56 „
Difference	= 174·04 sec.
Multiplied by the factor k for capillary I. (0·01), gives the kinematic viscosity .. .. .. ν =	1·74 cSt.

If the capillary is selected by means of the auxiliary pipette, the correction, as given in the table, will be an underlined value, and the error will not exceed $\pm$ 0·1 per cent. When using the corrections not underlined, the error will be at most 0·2 per cent., except that this is exceeded in the case of corrections in parentheses.

[47] One may interpolate in the table to increase the accuracy of work.

When it is desired to give evidence of the correctness of the results, the instrument and the number of the capillary (I., II. or III.) should be mentioned.

Correction table (see Note 41).—The table contains the corrections in seconds which are to be subtracted from the observed times of flow :—

TABLE II.

Observed time of flow. Sec.	Corrections in seconds, for capillary I. Sec.	II. Sec.	III. Sec.	Observed time of flow. Sec.	Correction in seconds, for capillary I. Sec.	II. Sec.	III. Sec.
20	(14·0)	(1·40)	0·14	100	2·81	0·28	0·028
25	(11·2)	(1·12)	0·11	120	2·34	0·23	0·023
30	(9·4)	0·94	0·09	140	2·01	0·20	0·020
35	(8·0)	0·80	0·08	160	1·75	0·18	—
40	(7·0)	0·70	0·07	180	1·56	0·16	—
45	(6·2)	0·62	0·06	200	1·40	0·14	—
50	(5·6)	0·56	0·06	250	1·12	0·11	—
55	(5·1)	0·51	0·05	300	0·94	0·09	—
60	(4·7)	0·47	0·05	350	0·80	0·08	—
70	(4·0)	0·40	0·04	400	0·70	0·07	—
80	(3·5)	0·35	0·04	450	0·62	0·06	—
90	3·1	0·31	0·03	500	0·56	0·06	—

The conventional values for the Engler, Redwood or Saybolt instruments, corresponding to the kinematic viscosities, may be taken, without calculation, from the International Viscometer Tables.[48]

The dynamic viscosity η in centipoises (cP) is calculated from the kinematic viscosity ν by the formula :—

$$\eta = \nu\rho \ (\rho = \text{density at temperature of test}).$$

The density is usually fairly well known. If it is not known at the test temperature, it may easily be calculated for mineral oils from the average co-efficient of expansion (increase in unit volume for a rise in temperature of 1° C ; see Table III.).

By using the above formula smaller errors will usually be made than in direct determination of dynamic viscosity.

TABLE III.

Density.		Coefficient of expansion for 1° C.
0·690–0·730	..	0·00085
0·730–0·760	..	0·0008
0·760–0·790	..	0·00075
0·790–0·830	..	0·0007
0·830–0·920	..	0·00065
0·920–1·000	..	0·00062

[48] "Internationale Tabellen für Viskosimeter," by Ubbelohde, 1933. Karlsruhe (Baden), Germany, as the 4th edition of "Tabellen zum Englerschen Viskosimeter." Concerning their basis, see Mitteil. der Intern. Petroleum Kommission, publications of the I.P.K., Nos. 18,610 and 18,627, and *Petr. Z.*, 1932, **28**, Nos. 3 and 17.

Emptying and cleaning the Instrument.—The thermometer is removed from tube 1, the frame is removed from the bath and hung inverted in a place where it can drain. When dripping ceases, the oil remaining in the instrument has been so reduced that there is no need of cleaning. If it is desired to save time, the instrument is allowed to drip for a short time, a preliminary amount of the next oil to be tested is drawn in, it is forced by alternative suction and pressure on the rubber tube in and out of C and A for a few times, and then allowed to run out, without being used, from the instrument hanging inverted. The mixture which then remains in the instrument contains so little of the first oil that it has no effect on the following measurement.

FIG. 13.

AUXILIARY PIPETTE FOR PRELIMINARY TEST.

If, however, it is necessary to clean the instrument thoroughly, a solvent is poured in, moved up and down as above described, emptied out, and then the instrument is dried by the use of suction. In changing from tests with watery solutions to oils, the instrument is first washed with benzole, but when changing from oils to watery solutions, it is best to use benzole, alcohol and diluted soda lye and water in the order named.

Advantages of the Viscometer.—The viscometer is more accurate than any other similar instrument, actually as accurate, as the time can be measured in which the meniscus falls from the upper to the lower mark on the pipette, in which ordinarily errors

greater than 0·1 per cent. do not occur. The much larger errors, unavoidable with other viscometers, due to incorrect adjustment of pressure, etc., disappear.

The operation is incomparably easier, quicker and more certain than with other efflux instruments, and an error is scarcely possible for the following reasons.

It is not necessary to pour in a definite volume of liquid; only 8 to 10 cm.³ are required.

The pressure head adjusts itself with physical certainty and is independent of the temperature.

Check tests can be made without pause or delay; the pressure head does not get out of adjustment as with other instruments.

All calculation is avoided.

2. *Viscometers for the Direct Determination of the Dynamic Viscosity.*

Principle and Method of Operation.—As a rule, it is of advantage to determine the kinematic viscosity ν and to calculate the dynamic viscosity η from it by multiplying by the density. In this case the previously described hydrostatic head instrument can be used, and it operates with essentially greater certainty than the following apparatus, complicated by the external pressure regulator.

Only where it is necessary to obtain the dynamic viscosity directly or to search for indications of flow-elasticity is it unavoidable to use instruments with external pressure regulators.

The old double-bulb instrument, Fig. 14, of the author [49] was filled with the liquid under test so that it at first extended from c to d_1, then pressure was applied at c and the liquid forced into the other bulb. Since both bulbs lie at the same elevation, and the difference in liquid level in the two is transposed in the course of the test, all effects of hydrostatic head and density of the liquid are counterbalanced. This holds exactly only in the regime of Poiseuille's simple equation, not in the regime of the Hagenbach correction in which density must be considered.

Now it is always troublesome to fill the instrument exactly from c to d_1, and since in investigations in colloid chemistry it is recommended by several authors and is much used, it appeared worth while to make it more convenient by means of the suspended

[49] The capillary of the instrument is described in Ubbelohde's "Handbuch der Oele und Fette," 1st edition, 1908, Vol. 1, p. 340. Also in Hatschek, "The Viscosity of Liquids," and in its German edition (Theodore Steinkopf, 1929, Leipzig, p. 28). Also by Guy Barr, "A Monograph of Viscometry," p. 108, 1931. The capillary and the original form of pressure regulator are described in Engler–Höfer, "Das Erdöl," 1st edition, 1916, Vol. 4, p. 109, and 2nd edition, Vol. 4, p. 30; also in Houben, "Organische Arbeitsmethoden, 3rd edition, Vol. 1, p. 1199; and, finally, with a different pressure regulator, in Holde, "Untersuchungen der Oele und Fette," all editions since 1908.

level. This resulted in the design shown in Fig. 15, which, however, is difficult to clean, since the instrument cannot empty completely, no matter how it is hung (see page 410). This disadvantage, however, can be removed by adding the dotted tube 7, keeping it closed during a test by the cap 8. To drain the instrument the cap is removed and the instrument hung up inverted.

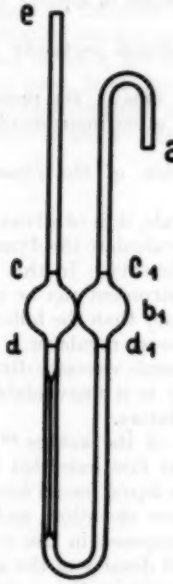

FIG. 14.

DOUBLE BULB VISCOMETER FOR MEASURING η DIRECTLY.

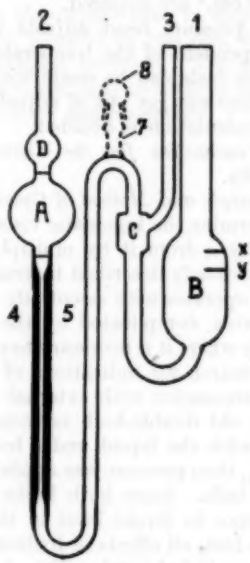

FIG. 15.

NEW VISCOMETER FOR MEASURING η DIRECTLY.

The instrument is filled through tube 1 with the test liquid until its meniscus lies between the two marks x and y on the bulb B. Then tube 3 is closed by the finger and suction applied at 2 until the liquid has filled C, 5, 4, A and D in turn. If tube 3 is now opened, a suspended level is formed in C. The elevation of the suspended level is so arranged that it is at the middle of A. Then, in viscosity measurements, the meniscus in A moves from one side to the other of the middle position, so that the density of the test liquid does not enter into the calculation. The instruments are also supplied with frames (Fig. 11) and fit in thermostats (Fig. 12).

Calculation of Results and Calibration of the Instrument.—With both instruments of Figs. 14 and 15 the density of the liquid remains out of consideration (but compare page 412), so that the calculation of dynamic viscosity is reduced to the simplest equation

$$\eta = p\,t\,k.$$

In this formula, derived from equation (1), t is the time of flow, p the pressure (outside pressure) and k the calibration constant. The formula requires that the product of pressure times time of discharge shall be constant, that is, $pt = p_1 t_1$. This, however, assumes constant volume, and applies only when the same pressure is used in calibration and in use.[50]

The following may perhaps be added. Both in publications [51] and elsewhere the opinion is widespread that with liquids of high viscosity a larger amount remains in the container of the viscometer that in the case of liquids of low viscosity, and that therefore there is a loss in the accuracy of the test. However, this does not agree with the facts; for it may be derived from my formula that the remaining volume V_x is independent of viscosity [52] if the time of flow is proportional to the kinematic viscosity, that is if $\frac{\nu}{t}$ is constant, which holds with all instruments which operate without external pressure, or always with the same pressure p.

We shall pass over the theoretical derivation and rather give a practical test. An instrument like Fig. 1 was used in the test, but it had a very short capillary, and the liquid was allowed to flow out under its hydrostatic head. Two very different oils—namely, light gas oil and a lubricating oil of 15 times its viscosity (cSt)—were tested. At the moment when the meniscus reached the mark m_2 the instrument was placed in a horizontal position so that the flow was stopped. It could be determined by weighing that the same weight of both oils remained.

If it is desired to work with different pressures—and with this instrument that is the rule, and, indeed, is unavoidable in determining structural elasticity—it is to be taken into account that so much more liquid remains in the viscometer, the more the time t is decreased by raising the external pressure p. Therefore,

[50] With the apparatus of Fig. 14 this is always the case if it is used so that the liquid flows into the second bulb which is completely dry before the test, but this is too inconvenient on account of the continual cleaning necessary.

[51] Engler–Höfer, "Das Erdöl," 2nd edition, 1930, Vol. 4, p. 32, and many other places.

[52] This rule, derived from the hydrodynamic formulas, naturally applies without restrictions only so long as do our hydrodynamic assumptions—therefore they do not apply after the boundary layers become so thin that they approach molecular dimensions, which, however, can hardly occur here.

the volume V_s remaining in the viscometer must be eliminated by calculation. From the equations above given (2 to 5) it is easy to show that V_s increases much slower than the pressure p; but the numerical value is hard to obtain because the instrumental constants depend on uncontrollable size and slope of the inner walls of the instrument. But the correction is easy to determine experimentally, by calibrating the capillaries with different pressures; the function of p thus obtained then applies, with the tested instrument, for all liquids of different viscosities, since the thickness of the adhering layer is the same for all liquids (but compare Note 52).

3. *Pressure Regulator with Suspended Level.*

For the instruments Figs. 14 and 15 a variety of pressure regulators may be used. That of the author,[53] as furnished with

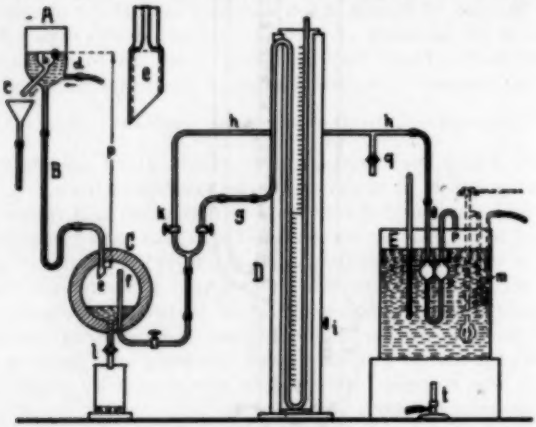

FIG. 16.

PRESSURE REGULATOR.

the suspended level, is shown in Fig. 16. The admission of water is so regulated at d that it flows from the upper container A in a moderately large amount through the small overflow b into the waste pipe c. The valves l and k are kept closed. By raising or lowering the upper container A, the desired pressure is produced in the air vessel c and is read on the water manometer D.

At the lower end of the tube B, through which the water flows from A to C, there is introduced a suspended level, as shown at e in the enlarged separate sketch; otherwise there is always formed at this place a curved liquid surface and drops which cause

[53] See note 49.

oscillations of pressure. Also the upper overflow b does not always function regularly because the water poorly wets the rim of the overflow. This trouble, however, is removed by a U-shaped wire covered with thick woollen threads, which hangs over the overflow and keeps the upper liquid level constant by capillary action.

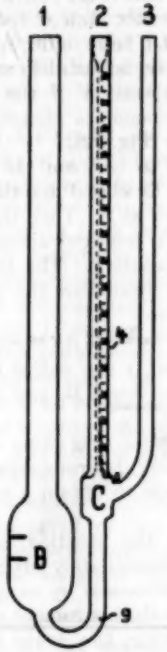

FIG. 17.
APPARATUS TO MEASURE CAPILLARY RISE (3/10 SIZE).

4. *Apparatus to Determine Surface Tension by the Capillary Rise Method.*

The usual apparatus for determining the capillarity constant by the capillary rise method resembles the Ostwald viscometer. The rise in the capillary is determined by measuring the difference in elevation of the meniscus in the capillary and the liquid surface in the container. Here evidently the same difficulties are met with as in viscosity measurements. Therefore Michaelis [54] has already recommended, instead of determining a difference in

[54] Michaelis, "Praktikum der physikalischen Chemie," 1921, p. 61.

elevation between a meniscus and a liquid surface, to dip in the liquid to be tested capillaries of different diameters, firmly joined together, and to read the difference in elevation of the menisci in the two, since this difference is proportional to surface tension. It is easier to avoid the difficulty by means of the suspended level. The apparatus suited for this (Fig. 17), whose theory has already been considered on page 399, differs from the new viscometer (Fig. 10) only in that the large bulb A above the capillary is missing, and the capillary is smaller and carries a millimeter scale with zero at the elevation of the suspended level. Like the viscometer, the instrument is enclosed in a frame (Fig. 10) and fits in the thermostat (Fig. 12).

The apparatus is filled to between the two marks x and y on the lower vessel, tube 3 is closed by the finger, and the oil is drawn up into the capillary at 2. Then the finger is removed from tube 3 and the vacuum is removed simultaneously from 2. The liquid then falls in the capillary. The height at which it stands is read on the scale and from this the capillarity constant a is calculated by the formula—

$$a = 1/2\, h\, r\, \gamma.$$

Here h is the rise in mm., r the radius of the capillary in mm., which is engraved on the vessel B, and γ the specific gravity at the temperature of test.

Also, with the viscometer (Fig. 10), a might be determined before or after the viscosity determination, except that in general the capillaries are too large to obtain a sufficiently large capillary rise.

With volatile liquids the position of the meniscus in the capillary must be read immediately after it becomes established, since the capillary rise decreases by evaporation. Also, it is not to be recommended to let the instrument stand long before reading, for if disturbed by shaking, the lower surface could be arched upward and thus the meniscus fall in the capillary, by a certain though small amount. At least, with narrow capillaries, trouble is caused by the fact that air bubbles are easily formed when the liquid is drawn up, for which reason perhaps this instrument is not so generally applicable as the viscometer.

In this instrument we were still concerned with the suspended level, which was flat and did not have to be considered in making the measurement. This is not the case in what follows.

5. *Dynamic Surface Tension and an Instrument to Determine It.*

In the theoretical chapter (page 384) we could consider the liquid as if its molecules were uniformly distributed throughout the whole liquid. In the present section hydrodynamics is of less importance than surface tension effects, which occur in layers

of a material nature as a consequence of the orientation of the molecules due to the molecular fields of force. This stratification appears to be connected with the expiration of time, and changes the surface tension. Lenard[55] was the first to thoroughly consider this phenomenon theoretically, and he investigated it in rapid movement by the method of oscillating drops or by observing the capillary rise when the surface was sprayed.

My dynamic method furnishes a new means of making this measurement; it is only necessary, instead of preventing as before the arching of the surface and thus eliminating its pressure effect, to increase it by a suitable size and form of the capillary outlet. Also, the velocity of the surface formation may be varied by changing the size of outlet and the velocity of flow. The surface tension may then be measured in two ways:

1. Dynamically, because the back pressure, and thus the time of flow, must vary with the magnitude of the surface tension.

2. Statically. If capillary 5 branches off near the outlet opening *a* of capillary 4, and capillary 5 is expanded into a larger tube 6, then every change in surface tension at the end *a* of the capillary must change the static pressure in tube 6.

Thus static and dynamic tests can be made simultaneously. The concave mouthpiece *a* as in Fig. 18 would cause an increase in effective pressure, and a convex mouthpiece as in Fig. 19 would cause a back pressure. The form of such an instrument must be suited to the test material and purpose. With suitable curvature the action can be treated mathematically; only when the flowing film is so thin that the effect of the molecular fields of force predominates at the liquid-solid interface, the problem becomes very complicated but also essential for a clearer comprehension of the subject.

The instrument may easily be calibrated for zero surface tension effect. The concave or convex mouthpiece may be exchanged for another which is flat and therefore has no pressure effect (suspended level, page 386), or (better) the pressure effect of the curved mouthpiece can be eliminated by dipping it in liquid and operating alternately, as described on page 399. If it is inconvenient to have the outlet of the regulating tube 3 near *a*, the tube may be omitted and the bottom of the large tube C cut off at an angle.

[55] Lenard, "Probleme komplexer Moleküle," Sitzungsberichte der Heidelberger Akademie der Wissensch. Mathem. Naturw. Klasse 5A; papers Nos. 27, 28 and 29; 1914. The quick changes after a surface is freshly formed were also investigated by E. O. Seitz, *Ann. der Physik*, 1929, **1**, 1099. See also "Variations in the Surface Tensions of Solutions," *J. of Phys. Chem.*, 1928, **32**, 320. Lenard, on the basis of his entire experience, examined as regards accuracy the already very many methods for measuring surface tension, in *Ann. d. Physik*, 1924, **74**, 381.

In this case the suspended curved level is formed by air entering C from below, as soon as the end of the tube is raised out of the liquid in a vessel placed below it.

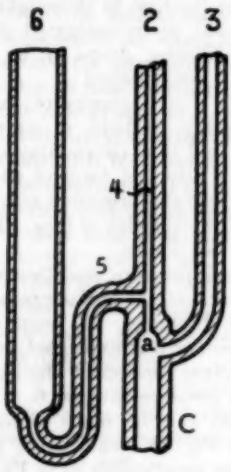

FIG. 18.

FIG. 19.

SCHEME FOR AN INSTRUMENT TO MEASURE DYNAMIC SURFACE TENSION.

The new test method might perhaps serve for the study of anisotropic surface tension in the sense used by Wo. Ostwald.[56] With rod-like dispersoids or mesomorphic states of matter, rod-like molecules could spread out in the suspended surface parallel to the circular solid surface after passing through the capillary, and thus show a variation in surface tension, while perhaps other methods of operation could give other kinds of surface tension.

With mineral oils the surface tension, and especially its variation with time, should be of interest on account of its relation to intrinsic pressure, compressibility, absorption velocity, dielectric constant and related values, and also new conceptions of semi-dry friction (also a problem of flowing films) may be reached. I shall have more to say on this problem, which I have previously considered.[57]

6. *Remarks on the Construction and Calibration of the Instrument.* However simple the instruments are there are details which have not been mentioned to save space, but must be considered

[56] Wo. Ostwald, "Die Welt der vernachlässigten Dimensionen," 9th to 10th editions, pp. 164 and 168, and *Kolloid Z.*, 1932, **61**, 249.
[57] See note 1, "Theorie der Reibung."

in manufacture. The building of the instruments has therefore not only been placed in the hands of a firm recognised for such work, the Union Apparatebau Ges. Ltd., Karlsruhe (Baden), but it is also supervised.

Every instrument has the number etched on it of the accompanying certificate. The firm calibrates the capillaries by special devices, if calibration by the Physikalisch-Technische Reichsanstalt is not required. The instruments and method of adjustment are protected by German and foreign patents.

Originally the viscometer (Fig. 10) was simpler, that is, open from below. I have to thank Engineer C. Walther for causing me to build the model closed below. For the photographs I am indebted to my colleague for many years, Dr. Joh. Bartsch, and I thank Engineer M. Kemmler for assistance with some of the calculations and drawings.

IV. Summary.

As a constant of materials, and on account of its relation to the theory of fluids, viscosity has an increasing significance with which the accuracy of our viscometers has not kept pace. It is shown by a critical examination that even the best instruments in use show defects which cannot be eliminated by the usual means.

A previously unobserved *phenomenon*, however, the *suspended level*, offers a possible remedy. This refers to an entirely new principle of significance beyond the bounds of viscometry, and therefore it was first considered by itself, theoretically and experimentally, and separately from the original subject. Its theory, for which no adequate scientific basis could be found, had first to be developed; this therefore takes up a great part of our paper, and contains applications to laminar flow, surfaces and thickness of suspended liquid layers in dynamic and static equilibrium. Theory as well as experiment led to the here fundamental proof that the *location and action of the suspended level is independent of all variable characteristics of liquids*—viscosity, surface tension, specific gravity—and is the same for all liquids; and that it *adjusts itself with physical certainty*. Thus the level becomes an ideal aid in many hydrodynamic and static measurements, of which some are considered in the paper without exhausting the possibilities.

Applied to the viscometer, it resulted in a new type of instrument which has a suspended level in place of the usual lower liquid surface. Thus by its aid viscometers are freed from previously unavoidable errors in the adjustment of the lower liquid surface, and there was developed, with the aid of a simple air inlet tube, by means of which the suspended level can be formed at will, an instrument of unsurpassed simplicity and pre-eminent accuracy.

The correction for kinetic energy alone remains troublesome. This is necessary with all previously known instruments, and yet has often been neglected, although errors could thus arise that are greater than all others, and even make the instrument unserviceable when it is seen how difficult it is to apply the correction. The next object, therefore, was to avoid this difficulty, and this was attained by a new kind of dimensioning which fixed the value of the correction once for all, and made it possible that it was only necessary to multiply the corrected time of discharge by a power of 10, *i.e.*, to move the decimal point, in order to obtain directly the *kinematic viscosity* in centistokes.

To make the dimensions of the viscometers accurate enough was accomplished by a special procedure which makes it possible to keep the dimensions within a hundredth of a millimeter. Everything together produced an instrument that is so easy to use and so thoroughly eliminates all errors that in the future it would be hardly excusable if viscosity data of dubious value are obtained.

The conversion of kinematic viscosities into the *conventional units* of the Engler, Redwood and Saybolt instruments may be accomplished by a table, while the dynamic viscosity is obtained from the kinematic by multiplying by the density. An instrument was also built for the direct determination of *dynamic viscosity*, making use of an older instrument of the author which is much used in colloid chemistry to determine structural elasticity. Also, by use of the suspended level, the pressure regulator necessary with this instrument could be free from the previously unavoidable pressure oscillations.

With the well-known instruments for measuring *static surface tension* by the capillary rise method also, the lower liquid surface was replaced by the suspended level and the accuracy thus increased.

Attention was then transferred from the field of hydrodynamics to interfaces. By applying the laws of flat surfaces found in the theoretical part, to purposely curved liquid films, a new method has been found for measuring *dynamic surface tension* and thus to seek out layers of a material nature, anisotropic arrangements of molecules and related phenomena at interfaces; questions which it is important to explain, not only in biology and investigations of structure, but also in practical bearing friction, which is also a problem of the flowing film.

It is naturally suggested to combine the method of investigating liquid—gas interfaces with one for liquid—solid interfaces, and I hope shortly to be able to present a paper on this subject.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND FIFTY-FIRST GENERAL MEETING of the Institution of Petroleum Technologists, held at the House of the Royal Society of Arts, John Street, Adelphi, London, W.C., on Tuesday, May 9th, 1933, the Chair being occupied by the President, Mr. T. Dewhurst, A.R.C.Sc., F.G.S.

The Secretary read the names of the candidates nominated for election, and the following list of members elected :—

As Members.—Nils Olaf Backlund, Robert T. Haslam, Stig Beskow, John Peter Mitchell, Archibald Henry Richard.

As Transfer to Member.—Arthur Thomas Wilford.

As Associate-Members.—Donald Bartleman Booth, Francis Alfred John Cole, Edward Thomas Marshall, Auguste William Pottier.

As Transfer to Associate-Member.—Adolph Freiman.

As Student.—Edward Albert Baker.

The President announced that, in accordance with the Bye-Laws, section 7, paragraph 6, the Council had decided to co-opt Mr. Elliott A. Evans and Mr. James Romanes as ordinary Members of Council. Dr. A. Wade had been appointed Honorary Librarian and Mr. George Sell Librarian.

Proceeding, the President said that as the present meeting was the last general meeting of the Institution before the Congress, which would open on July 19th, the Council had felt that advantage should be taken of the opportunity of explaining to the members the present position in regard to the Congress and of discussing probable developments.

The decision to hold a World Petroleum Congress had been taken during Mr. J. Kewley's term of office as President, and Mr. Kewley naturally became Chairman of the Congress Committee, and he (the President) could not do better than ask Mr. Kewley to explain the present position of the Congress arrangements.

Mr. J. Kewley remarked that the international nature of the petroleum industry, and the enormous strides which it had made during the last few years, made the holding of such a Congress as the one proposed very desirable.

During the last twenty years very great changes had taken place in the petroleum industry. For example, Venezuela, Persia, the Argentine, Sarawak, Columbia and Egypt had all come into production, many new fields had been developed in the United States, and production had been enormously increased in a number of other countries. Aerial photography and geophysics had come

to the assistance of the geologist, the introduction of rotary drilling had taken place, and other new methods of raising oil had completely changed the technique of production.

In the refining industry the changes had been quite as marked. The old cylindrical still had given way almost entirely in all modern plants to the tubular still with fractionating columns, and the cracking industry had practically developed in that time. Natural gas, which in those days had been a waste product, was now the basis of a great and important industry.

Together with this development had also grown up a very much higher standard in quality of products. The need for closer definition of pure products had arisen, and the international use of these products demanded some international understanding of their nature.

The need for a World Congress on technical matters was obvious, and its work fell into two main categories: (1) a discussion on matters of general technical interest, particularly new developments and problems; and (2) an endeavour to bring about some measure of international agreement on such points as methods of testing and nomenclature.

The need for agreement in testing methods was universally recognised and found expression in the attention it received from such bodies as the Union Internationale de Chimie, the World Power Conference, and many national standardizing bodies. It was very gratifying to be able to report that Committee 28 of the International Standards Association was arranging for its inaugural meeting to be held in London during the Congress. Dr. R. P. Anderson, the Secretary of that Committee, would be in attendance at the Congress, not only as the representative of the International Standards Association but also of the American Petroleum Institute.

He was very pleased to be able to report that His Majesty's Government had given the Congress its recognition, and the interest which the Ambassadors and Ministers of certain foreign countries were taking in the proceedings was very welcome.

The membership of the Congress was steadily increasing, and in the last week over 30 new members had been enrolled.

Arrangements were also being made for a series of small exhibits in the Imperial College of Science and Technology, such as the development of the petroleum lamp, the development of the candle, and geophysical apparatus. An opportunity might also be afforded of demonstrating any new apparatus, and in the laboratories of the various companies demonstrations would be made of various types of testing apparatus.

Dr. A. E. Dunstan said that the members had before them the tentative programme, and from this they would see that a

series of General Reporters had been appointed. Their duty would be to collect papers, to edit them, and to present a summary of them at the meetings of the Congress. These gentlemen were taking the keenest interest in their work, they had approached the world's experts in their particular field, and had secured promises of over 150 papers of the highest standing.

Mr. Kewley had alluded to the question of standardization. That was possibly the keystone of the arch of the Congress, and, if nothing else happened but that the Congress was able to bring about an international agreement on certain specified tests, it would have done its work and performed its function.

Professor J. S. S. Brame said that he would particularly emphasise that the real object of the calling of the Congress into being was to discuss International Co-operation in Standardization.

Those concerned with the Congress had been fortunate in having the very hearty co-operation of Dr. L. Ubbelohde, who had been associated with the work of the Internationale Petroleum Kommission for many years, and the Congress was receiving very useful support from that direction.

Reference had also been made to the United States, and particularly to Dr. R. P. Anderson, who was the Secretary of the Committee dealing with petroleum products as part of the International Standards Association. The first meeting of that Committee was to be held in London at the time of the Congress and was going to be a factor of very great importance. It would only be hoped that certain lines of action would be agreed upon with regard to international co-operation at that private meeting, and that definite submissions would then be made to the Congress in public session for full discussion.

As most of the members appreciated, the Institution worked in close co-operation with the British Standards Institution, and in the main the methods of test which had been recommended by the Institution's Standardization Committee had been adopted by the British Standards Institution. He felt that the very cordial relationship which existed between those two bodies was a matter for congratulation, and the same applied to the American Society for Testing Materials. It could only be hoped that a far greater extension would be possible when they got together with the other countries concerned.

Mr. Ashley Carter said that through the courtesy of the Governing Body and the kindness of the Rector, Mr. H. T. Tizard, arrangements had been made for the meetings of the Congress to be held at the Imperial College of Science and Technology, South Kensington.

The arrangements for the various social functions were well in hand and a special Ladies' Committee had been formed to look after the comfort and interests of ladies accompanying the delegates and members of the Congress.

Those responsible for the arrangements of the social functions would like to know as soon as possible the approximate number of persons who wished to take part in them, and he expressed the hope that those who wished to join the Congress, but who had not yet done so, would send their names and the fee of 10s. to the Secretary as soon as possible. A questionnaire would be circulated within the next few days and the prompt return of this would be of great assistance.

Mr. C. H. Gray (World Power Conference) said that the World Power Conference warmly welcomed the Congress, and in particular the Standardization Section. At the 1932 meeting of the International Executive Committee of the World Power Conference a small committee had been appointed to examine the whole position regarding standardization of testing methods, and the report of Dr. A. E. Dunstan, as chairman of that committee, would be presented to the Congress for discussion. The whole of the Standardization Section was of great general importance and he expressed his confident expectation that the Congress would be extremely successful.

Mr. C. Le Maistre (British Standards Institution) said that the question of international agreement on tests, terms and definitions was of vital interest. It implied international agreement to speak the same technical language, to give some means whereby one could compare the tests carried out in different countries, and also to give some method of appraising the value of the product itself, without necessarily going into the question of specifications. He and his Institution recognised the necessity of the petroleum industry obtaining international agreement on such matters.

Mr. P. C. Pope (Institute of Fuel) said that his Council would do everything they could to assist the Congress.

Mr. W. H. Howe (National Federation of Lubricating Oil and Grease Manufacturers) said that he particularly welcomed the Congress, more especially from the lubricating side, because it was agreed that the subject of lubrication had now become highly scientific.

Mr. W. H. Bateman said that the Congress would afford an opportunity, which had not arisen before, of bringing together users and designers of equipment in this country, and he felt that much good would come if contributors to the discussion in the

various sections would state their experience of the performance of equipment and also the directions in which they looked for improvement in the future.

Mr. J. Kewley, in replying to the discussion, said that the various points raised would be considered by the Congress Committee.

He also expressed his thanks to the Oil Industries Club, who had very kindly offered to assist in the entertaining of the foreign visitors to the Congress.

The President, in closing the meeting, said that any written communications sent to the Secretary would receive full consideration by the Congress Committee.

CORRESPONDENCE.

TO THE EDITOR. May 9th, 1933.

Sir,—"**The Migration of Oil and Natural Gas,**" Prof. V. C. Illing, *J. Inst. Petr. Techn.*, 1933, **19**, 229–274.

In the above paper full credit is not given to a Member of the Institution by the bare reference in the Bibliography to "10. Stuart, Murray," etc., particularly as during the discussion at the meeting Prof. Illing said (not published) that, as Munn's work was prior to Murray Stuart's, he had given Munn the credit for it.

The work of the two was completely different. Munn's results were apparently not based on any experiments, but on deductions from incorrect premises, whereas Murray Stuart's results were arrived at from considered arguments founded upon careful experiments, which proved the incorrectness of Munn's chief hypothesis.

The reference to Munn's work in Murray Stuart's paper (*Rec. Geol. Surv. India*, 1910, **40**, 331–333), and particularly the final paragraph, is a correct, though very mild, way of putting the difference.

Surely more credit is due to Murray Stuart than to Munn.

T. R. H. GARRETT.

BOOK RECEIVED.

CHEMICAL ENGINEERING AND CHEMICAL CATALOGUE. 9th Edition. Edited by D. M. Newitt. London: Leonard Hill, Ltd. Pp. 281+lxxii.

The ninth edition of this annual reference book and manufacturer's catalogue follows the form of previous editions. The first section consists of a catalogue of chemical plant and products, followed by indices to advertisers, to the suppliers of various commodities, and to trade names and marks. A special section is devoted to the English equivalents of Spanish technical terms and should prove of great value to anyone having dealings with Spanish-speaking countries.

The table and data section contains data relating to structural materials, treating methods, physical properties, etc., and forms a valuable source of information for the chemical engineer.

The last section of the book contains a very comprehensive bibliography of technical works, and is very conveniently sub-divided into subjects.

The volume is very well printed, and the use of a thinner paper has reduced its bulk as compared with previous editions.